



# EERC

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December 23, 2003

Ms. Lynn A. Brickett  
U.S. Department of Energy  
National Energy Technology Laboratory  
PO Box 10940, MS 922-273C  
Pittsburgh, PA 15236-0940

Dear Lynn:

Subject: Final Report, "Selective Catalytic Reduction Mercury Field Sampling Project, 2002";  
DOE Cooperative Agreement No. DE-FC26-98FT40321; UND Fund 4712

Enclosed please find one copy of the subject EPRI report, which includes research performed under JV Task 36.

If you have any questions, please feel free to contact me by telephone at (701) 777-5138, by fax at (701) 777-5181, or by e-mail at [dlaudal@undeerc.org](mailto:dlaudal@undeerc.org).

Sincerely,

Dennis L. Laudal  
Senior Research Advisor

DLL/drh

Enclosure

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# **Effect of Selective Catalytic Reduction on Mercury, 2002 Field Studies Update**

**Product ID #1005558**

Final Report, October 2003

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## CITATIONS

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## PRODUCT DESCRIPTION

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This project was a joint effort between EPRI, the U.S. Department of Energy (DOE), and the U.S. Environmental Protection Agency (EPA).

### Results & Findings

Selective catalytic reduction (SCR) catalysts appear to assist in converting elemental mercury ( $\text{Hg}^0$ ) to oxidized mercury ( $\text{Hg}^{2+}$ ). This effect appears to be more likely to occur with bituminous coals, where 90+%  $\text{Hg}^{2+}$  is possible at the particulate control device inlet. The three bituminous coal-fired power plants tested with wet flue gas desulfurization (FGD) systems achieved mercury (Hg) removals of 84%–92% with SCR operation, as compared with 43%–51% without SCR operation. These increased removal efficiencies may be due to the combined effects of the SCR system to increase  $\text{Hg}^{2+}$  concentrations and reduce reemissions of the  $\text{Hg}^0$  from the FGD system. The effect of catalyst space velocity and age are not clear, but may have an impact on SCR Hg oxidation. The only Powder River Basin (PRB) site tested did not show a high oxidation rate. It is important to note that these findings are based on a relatively small data set and, thus, should be considered preliminary rather than final conclusions that can be extrapolated to predict the results at all other similar units. For example, two of the three FGDs tested were magnesium-lime systems, and the third FGD was a venturi scrubber; thus the combined effect of SCR and the most common FGD design of a limestone, forced-oxidation system has yet to be evaluated.

### Challenges & Objectives

The objective of this study is to evaluate the effect of SCR systems on Hg speciation and removal. The most significant challenges are the complexity of the Hg chemistry and the number of possible factors that may directly or indirectly affect Hg oxidation and removal. This, along with the challenges to accurately measure Hg, must be considered when the data are interpreted, and thus caution must be taken to extrapolating the results to similar untested power plants.

### Applications, Values & Use

The results will be used to help plan future control strategies as well as to assist in developing Hg regulations for coal-fired power plants.

### EPRI, EPA, & DOE Perspective

This report summarizes field measurements at six power plants with SCRs conducted in 2001 and 2002. These results indicate that SCRs can increase Hg oxidation and improve Hg removal in the downstream FGD. This effect appears to be more likely for bituminous coal applications, and the effect of catalyst properties such as space velocity and age is still somewhat unclear. Additional field measurements are being conducted in 2003 to better understand the effects of



coal properties and catalyst properties and to better characterize longer-term FGD Hg removal, including the possible impact of SCRs on Hg<sup>0</sup> reemissions across the FGD. Full-scale and sidestream tests are planned by this project team as well as in a separate DOE/Consol study to further evaluate the combined effect of SCRs and FGDs on Hg removal. To evaluate the effect of coal properties, measurements are planned at a pulverized-coal-fired power plant burning a PRB coal, with a second PRB site to be tested around January 2004. Additional follow-on tests to evaluate catalyst-aging effects are planned at the two power plants that indicated significant Hg oxidation in the 2001 tests and were retested in 2002. Tests are also being conducted at a power plant burning a blend of bituminous and PRB coals. Thus the results in this report should be viewed as work in progress, and the reader is encouraged to follow up and read future reports.

### **Approach**

Hg measurements were completed at four coal-fired power plants with SCR systems in 2001 and are summarized in EPRI Report 1005400. Additional measurements were conducted in 2002 at four plants with SCR, including two plants tested in 2001 that showed significant Hg oxidation. Speciated Hg concentrations in flue gas were sampled and evaluated using the wet-chemistry Ontario Hydro method, as well as near-real-time Hg semicontinuous emission monitors. Sampling was conducted at these plants at the inlet and outlet of the SCR reactor to evaluate the effects of SCR on Hg speciation, as well as the inlet and outlet of the particulate and SO<sub>2</sub> control devices to evaluate Hg capture. Additional sampling involved the use of selective condensation to measure sulfur trioxide and EPA Method 27 for ammonia slip. Fly ash, FGD solids, and coal samples were also collected to estimate the Hg mass balance across the control devices.

### **Keywords**

Mercury, Selective Catalytic Reduction, SCR, Ammonia, Air Toxics

## LIST OF ABBREVIATIONS

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AA	atomic absorption
AF	atomic fluorescence
CEM	continuous emission monitor (refers to plant systems)
CI	confidence interval
Cl <sub>2</sub>	chlorine
CO <sub>2</sub>	carbon dioxide
CVAA	cold-vapor atomic absorption
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
F <sub>d</sub>	emission factors calculated from coal analysis – dscf/10 <sup>6</sup> Btu
FGD	flue gas desulfurization
Hg	mercury
Hg <sup>0</sup>	elemental mercury
Hg <sup>2+</sup>	oxidized mercury
LOI	loss on ignition
MW	megawatt
N	normal is defined at 20°C and 1 atmosphere pressure
NH <sub>3</sub>	ammonia
NO <sub>x</sub>	nitrogen oxide
OH	Ontario Hydro mercury speciation
pc	pulverized coal
PM <sub>2.5</sub>	particulate matter less than 2.5 μm
PRB	Powder River Basin
PSA	PS Analytical
QA	quality assurance
QC	quality control
QMS	quality management system
Hg SCEM	mercury semicontinuous emission monitor
SCR	selective catalytic reduction
SG	Smith Greenburg
SNCR	selective noncatalytic reduction
SO <sub>3</sub>	sulfur trioxide
SSTP	site-specific test plan
TiO <sub>2</sub>	titanium dioxide
V <sub>2</sub> O <sub>5</sub>	vanadium oxide



# EXECUTIVE SUMMARY

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## Introduction

The objective of this report is to document the results and provide a summary of the 2001 and 2002 field tests associated with the "Selective Catalytic Reduction Mercury Field Sampling Project." The testing was sponsored by EPRI, with additional funds provided by the utility industry, the U.S. Department of Energy (DOE) National Energy Technology Laboratory, and the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory. Hg measurements were completed at six different power plants, four in 2001 and two in 2002, equipped with selective catalytic reduction (SCR). In addition, two of the plants tested in 2001 were retested in 2002 for a total of eight data sets. Testing was also conducted in 2001 at two facilities that employed flue gas conditioning to improve electrostatic precipitator (ESP) performance and one that used selective noncatalytic reduction for nitrogen oxide control.

Coal combustion by electric utilities is a large source of anthropogenic mercury (Hg) emissions in the United States, according to EPA [1]. Recent data indicate that the total Hg emission from coal-fired power plants in the United States is about 45 tons/yr [2]. EPA views Hg from coal-fired utilities as a potential public health concern [3] and, as a result, is currently involved in a rule-making process that would require Hg control for coal-fired electric utilities by 2008.

Hg emissions from coal-fired boilers can be empirically classified, based on the capabilities of currently available analytical methods, into three main chemical forms: elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ), and particle-bound Hg. These impending Hg regulations require that control strategies be investigated and developed. The efficiency of Hg control methods depends largely on the form of Hg (gas vs. particulate) and species of Hg (elemental vs. oxidized) formed upstream of the control devices. Particulate-associated Hg ( $\text{Hg}_p$ ) can be removed from flue gas by conventional air pollution control devices such as an ESP or a baghouse.  $\text{Hg}^{2+}$  compounds are readily captured in flue gas desulfurization (FGD) units.  $\text{Hg}^0$  is most likely to escape air pollution control devices and be emitted to the atmosphere.  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}_p$  concentrations are much varied in flue gas, depending on the coal composition, combustion conditions, and flue gas quench rate. Understanding the speciation of Hg is critical because control options rely heavily on Hg's form or species. The concentration of  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and particle-bound Hg in the flue gas primarily depends on coal composition and combustion conditions [4].

In addition to Hg, coal-burning power plants are a significant anthropogenic source of nitrogen oxide ( $\text{NO}_x$ ) emissions to the atmosphere.  $\text{NO}_x$  emissions are an environmental concern primarily because they are precursors to acid precipitation and are involved in atmospheric reactions that produce fine particles and ozone. The most common  $\text{NO}_x$  reduction strategy is the use of low- $\text{NO}_x$  burners. These burners have the capability of reducing  $\text{NO}_x$  emissions by 40%–

60%. However, with possible establishment of stricter ozone regulations, fine particulate ( $PM_{2.5}$ ), and regional haze, there is increased incentive to reduce  $NO_x$  emissions to a level below what can be achieved using low- $NO_x$  burners. SCR technology, which can reduce  $NO_x$  emissions by >90%, is, therefore, becoming more attractive, particularly because catalyst costs continue to decrease and the knowledge base for using SCR reactors is expanding. It is planned that approximately 100 gigawatts of coal-fired capacity will have SCR for  $NO_x$  by 2005 [5].

### ***Potential Impacts of $NO_x$ SCR on Mercury Speciation***

SCR units achieve lower  $NO_x$  emissions by reducing  $NO_x$  to  $N_2$  and  $H_2O$  in the presence of ammonia. These  $NO_x$  reactions with SCR are catalyzed by metal oxides such as titanium dioxide-supported vanadium pentoxide. These SCR units are operated at about 650°–750°F (340°–399°C). Pilot- and full-scale experience in both the United States and Europe has indicated that SCR catalysts promote the formation of  $Hg^{2+}$  [6–8]. Therefore, the use of SCR to reduce  $NO_x$  emissions has the potential to improve the Hg control efficiency of existing particulate removal and FGD systems by promoting  $Hg^{2+}$  formation. Possible mechanisms that could result in the SCR of  $NO_x$  impacting Hg speciation include:

- Catalytically oxidizing the Hg.
- Changing the flue gas chemistry.
- Providing additional residence time.

### **EERC Pilot-Scale Tests (conducted in 2000)**

In an attempt to evaluate the effects of SCR on Hg speciation, pilot-scale tests were conducted at the Energy & Environmental Research Center (EERC) [9]. The general conclusion reached based on these tests was that SCR has the potential to impact Hg speciation, but that the effects were coal-dependent. Because of the inherent concerns related to small pilot-scale tests (surface area-to-volume ratios, different flue gas chemistries, and time and temperature profiles), the project advisory and research team concluded it was necessary to conduct sampling at full-scale power plants. Therefore, EPRI, DOE, EPA, and a number of utilities began funding the EERC and other contractors to conduct Hg sampling at power plants with SCR technology.

### **2001 SCR Mercury Field Sampling Project**

The 2001 test program was developed to address the limitations of pilot-scale testing by applying information obtained from previous work to full-scale electric-generating facilities. In general, data from 2001 testing indicated that Hg oxidation can be enhanced by SCR operation, but the effect may be moderated by a variety of factors, including coal type, catalyst chemistry and structure, and space velocity. Significant differences in Hg speciation were observed among plants with similar coal classifications [8].

Four sites with SCR systems were tested in 2001. Three of these sites fired eastern bituminous coals and one a Powder River Basin (PRB) coal. Note that for purposes of this report, the PRB site is referred to as Site S1 and the other three as Sites S2–S4. However, because the PRB site used a cyclone boiler and was operated such that the ash contained a very high concentration of

unburned carbon, it was not considered representative of a typical PRB site. For the three sites that fired eastern bituminous coals, two of the three sites showed a significant increase in Hg oxidation across the SCR unit. These two sites resulted in 89% and 90% Hg removal downstream of an FGD system. The other test site fired a coal that generated a very high concentration of  $\text{Hg}^{2+}$ , at the economizer outlet, prior to SCR.

Upon review of the 2001 test results, it was evident that additional data would be necessary to quantify the effect SCR operation had on Hg oxidation given the diversity of power plant configurations and coal sources in the United States. The most important data gaps that were identified included the following:

- The effect of firing a PRB coal in a more typical configuration
- The effect of firing a low-sulfur compliance coal
- The effect of catalyst aging
- The effect of catalyst type and space velocity

In order to address some of these data gaps, the program was expanded, and additional testing was conducted in 2002. It should be noted that the highest priority was to test an SCR-equipped plant that fires a PRB coal. Unfortunately, no plant was available for testing in 2002 with this configuration. However, plans are being made to test two SCR-equipped PRB plants in 2003 and 2004.

### **Approach for 2002 Field Test**

The principal objective remained the same for the 2002 testing: determine the impact of SCR operation on Hg speciation and, ultimately, on Hg emissions. To achieve this objective for each unit/coal, a sampling plan was developed for various operating conditions so that the effects of SCR could be determined. At each site, tests were conducted (where feasible) under operating conditions with and without SCR in operation. This was done either by bypassing the SCR system or testing sister units, one with and one without SCR.

In addition to the effects of SCR operation, several other factors were identified as contributing factors to Hg oxidation and removal and were incorporated into the sampling plans for 2002. These factors included coal type, specifically chlorine and sulfur content, and catalyst age. A summary of the configuration of each plant is provided in Table ES-1 for 2001 and 2002 testing. Additionally, a summary of coal data for each plant is provided in Table ES-2.

Hg measurements were obtained using the manual Ontario Hydro (OH) method as well as Hg semicontinuous emission monitors (Hg SCCEMs). The sampling plans were set up to obtain OH samples at the SCR inlet and outlet, ESP inlet and outlet or, in the case of one plant, a venturi scrubber and at the stack. The Hg SCCEMs were used to measure Hg speciation primarily at the outlet of the particulate control device.

**Table ES-1**  
**Summary of SCR Program Plant Configuration**

Plant	Year Tested	Coal	Boiler Type	Boiler Size, MW	Low-NO <sub>x</sub> Burners	Catalyst Vendor And Type	Catalyst Age	SCR Space Velocity, hr <sup>-1</sup>	Particulate Control	Sulfur Control
S1 <sup>a</sup>	2001	PRB subbit.	Cyclone	650	No	Cornmetech honeycomb	2 ozone seasons <sup>a</sup>	1800	ESP	None
S2	2001	OH bit.	Wall-fired	1300	Yes	Siemens/Westinghouse plate	3 months	2125	ESP	Wet FGD
S2-2	2002	OH bit.	Wall-fired	1300	Yes	Siemens/Westinghouse plate	2 ozone seasons	2125	ESP	Wet FGD
S3	2001	PA bit.	Tangential-fired	750	Yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	None
S4	2001	KY bit.	Cyclone	650	No	Cornmetech honeycomb	1 ozone season	2275	Venturi scrubber	Venturi scrubber
S4-2	2002	KY bit.	Cyclone	650	No	Cornmetech honeycomb	2 ozone seasons	2275	Venturi scrubber	Venturi scrubber
S5	2002	WV bit.	Wall-fired	684	Yes	Halder-Topsoe plate	3 months	3700	ESP	Wet FGD
S6	2002	Low-sulfur KY and WV bit.	Concentric-fired	700	Yes	Cornmetech honeycomb	2 ozone seasons <sup>c</sup>	3800	ESP	None

<sup>a</sup> Not discussed in detail in this report.

<sup>b</sup> The ozone season is from May 1 through September 30.

<sup>c</sup> One layer of catalyst was replaced after one ozone season.

**Table ES-2**  
**Summary of Coal Analyses<sup>a</sup> for Plants Tested in 2001 and 2002**

	S1	S2	S2-2	S3	S4	S4-2	S5	S6
Mercury, $\mu\text{g/g}$ dry	0.10	0.17	0.14	0.40	0.13	0.18	0.13	0.07
Chlorides, $\mu\text{g/g}$ dry	<60	1333	523	1248	357/1160 <sup>b</sup>	270	472	1020
Moisture Content, %	27.5	7.6	6.1	7.0	10.5	8.3	4.6	6.1
Ash, %	3.7	11.7	9.4	14.0	9.1	9.1	12.1	11.6
Sulfur, %	0.19	3.9	3.9	1.7	2.9	3.0	3.6	1.0
Heating Value, Btu/lb	8960	11,092	12,097	11,421	11,341	12,077	12,120	12,019

<sup>a</sup> As-received unless otherwise noted.

<sup>b</sup> First value prior to bypass; second value postbypass.

## Description of Sites Tested in 2002

### Site S2

Site S2 was tested in 2001 and again in 2002 to collect data after an additional ozone season (May 1–September 30) of operation on the SCR catalyst. Unfortunately, a number of operational changes, including addition of SO<sub>3</sub> mitigation technologies and a change in the coal (as shown by the chloride values in Table ES-2), between 2001 and 2002 at Site S2 may have affected the results. In addition, operational problems occurred (plugging of the air preheater) at Site S2 in 2002 that resulted in a somewhat reduced test plan. The OH and Hg SCEM data were collected for the SCR on-line condition, but only Hg SCEM data were obtained for the SCR off-line condition.

### Site S4

Site S4 was tested in 2001 and again in 2002 to collect data after an additional ozone season of operation on the SCR catalyst. At Site S4, sampling was done with the SCR unit on-line followed by tests with the SCR unit off-line on the same unit. Based on Table ES-2, there was significant variability in the coal from one year to the next.

### Site S5

Site S5 was selected to provide additional data on the impact of SCR for a facility firing a high-sulfur eastern bituminous coal and utilizing a wet FGD system for SO<sub>2</sub> control. Hg sampling at Site S5 was done on two sister units: one with an SCR unit, the other without.

### Site S6

Site S6 was selected to represent facilities firing a low-sulfur compliance coal. Hg sampling at Site S6 was done on two sister units (one with SCR and the other with the SCR unit bypassed).



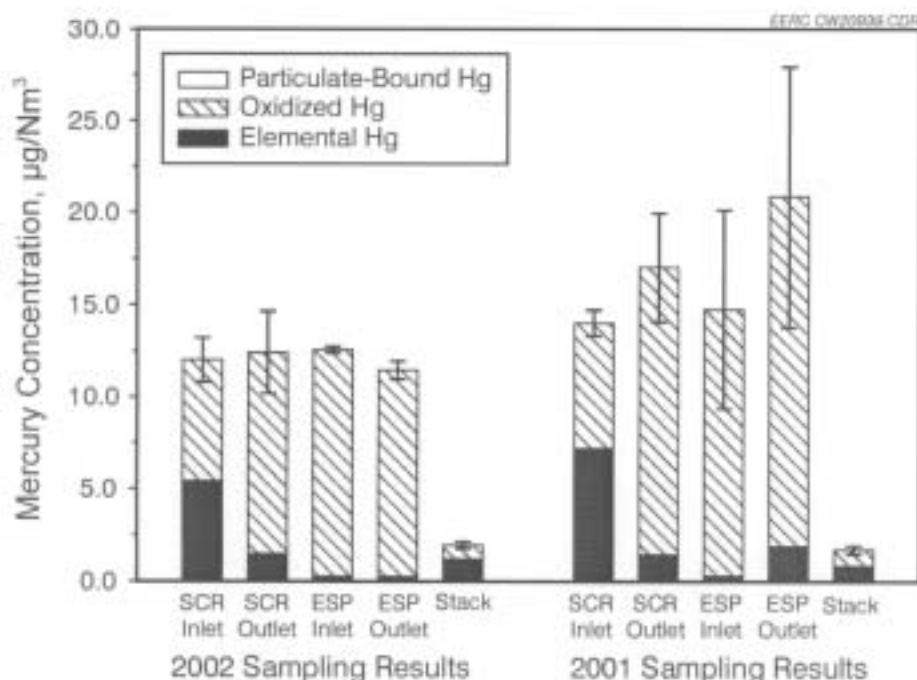
As part of another test program that was being conducted simultaneously with the SCR project, Hg sampling was also done at the stack of a third unit (no SCR).

## Mercury Emission/Capture Results for 2002 Field Tests

There were two primary objectives for the Hg testing in 2002. The first was to determine the Hg oxidation potential of the SCR catalysts at each test site. The second was to determine what impact SCR had on the Hg removal efficiency of each pollution control device. The overall Hg removal (unless otherwise specified) is defined as the Hg measured at the stack compared to Hg measured at the inlet to the particulate control device.

### Site S2

Site S2 was sampled in both 2001 and 2002 to determine the effect of operating SCR over an additional ozone season on Hg speciation. Units equipped with SCR are required to operate the SCR unit from May 1 to September 30 (ozone season) for plants burning bituminous coals, as is the case for Site S2. To evaluate catalyst aging on Hg speciation, the OH results for 2002 Hg sampling are compared to those obtained during 2001 testing. A summary of these results is provided in Figure ES-1. For this site, results show 54% and 48%  $\text{Hg}^{2+}$  at the SCR inlet for 2002 and 2001 sampling respectively. At the SCR outlet, oxidation of Hg across the SCR unit resulted in  $\text{Hg}^{2+}$  of 87% and 91% for 2002 and 2001, respectively. Comparing these results shows that the oxidation of Hg across the SCR did not significantly change from 2001 to 2002. This is also shown by comparing the ESP inlet sampling results, which was 97%  $\text{Hg}^{2+}$  for both years.



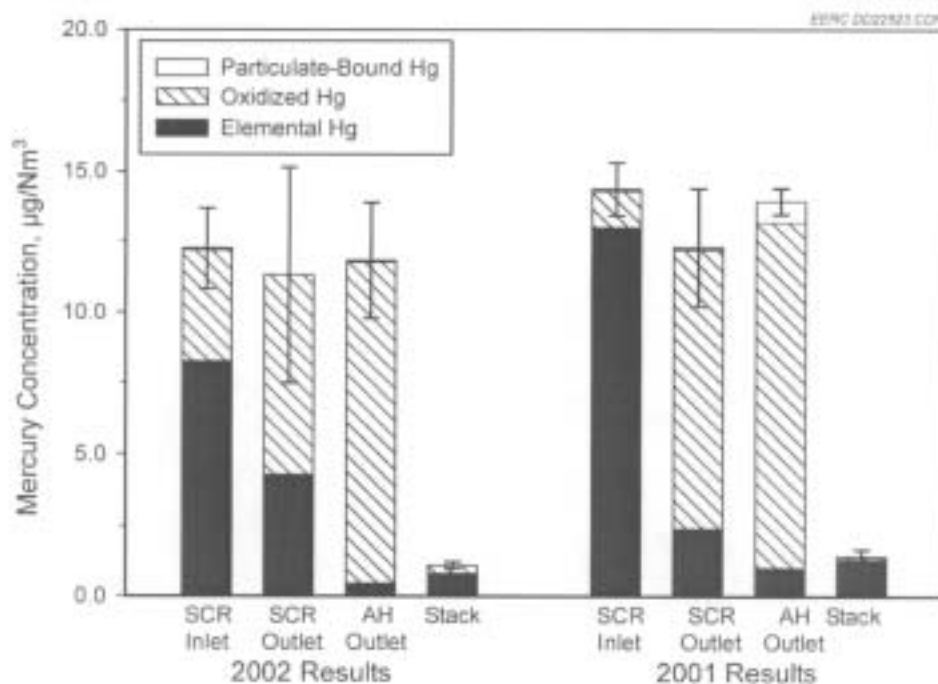
**Figure ES-1**  
**Mercury Results Comparing Speciation with SCR from 2001 and 2002 at Site S2**

The overall Hg removal in 2002 across the ESP and wet FGD was 84% compared to 89% in 2001. Operational problems at the plant prevented Hg sampling using the OH method with the SCR bypassed. Therefore, a comparison of Hg speciation with and without SCR was not possible using 2002 OH results. However, in 2001, Hg removal was only 51% when the SCR unit was bypassed.

The Hg SCEMs were operated at Site S2 for approximately 1 month and included the time the SCR unit was bypassed. Review of the  $\text{Hg}^0$  SCEM data illustrates an increase from  $<0.25 \mu\text{g}/\text{m}^3$  to approximately  $1.0 \mu\text{g}/\text{m}^3$   $\text{Hg}^0$  when the SCR unit was bypassed.

### Site S4

Site S4 was also tested in both 2001 and 2002. A comparison of the 2001 and 2002 results are shown in Figure ES-2. For this site, results show 33% and 9%  $\text{Hg}^{2+}$  at the SCR inlet for 2002 and 2001 sampling, respectively. At the SCR outlet, oxidation of Hg across the SCR unit resulted in  $\text{Hg}^{2+}$  of 63% and 80% for 2002 and 2001, respectively. Although this difference may have been attributable to a catalyst-aging effect, the coal fired at Site S4 varied, especially with respect to the chloride content. In 2001, the measured coal chloride content ranged from 350 to 1280 ppm and in 2002 was much closer, ranging from 240 to 300 ppm. Plant personnel indicated that the coal was from the same mine for both years. The information collection request coal analysis data from 1999 for Site S4 also indicated a wide range of chloride concentrations in the coal.

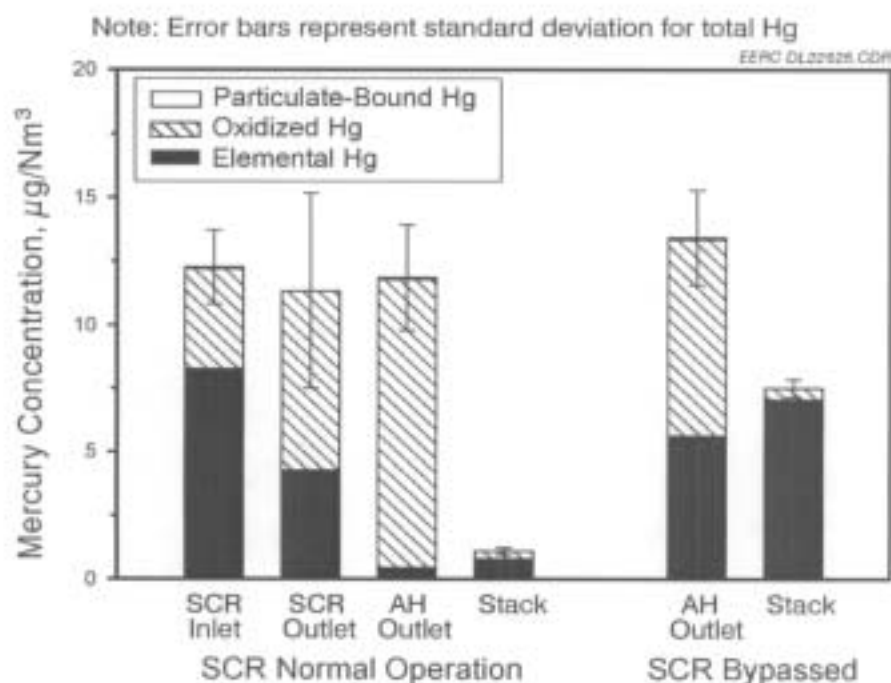


**Figure ES-2**  
**Mercury Results Comparing Speciation with SCR from 2001 and 2002 at Site S4**

Although there was a substantial decrease in Hg oxidation across the SCR catalyst between 2002 and 2001, downstream of the air preheater and just prior to the inlet of the venturi scrubber, there

was an increase in the percentage of  $\text{Hg}^{2+}$ . In 2002, 96% of the Hg was measured as  $\text{Hg}^{2+}$  at the outlet of the air preheater compared to 87% in 2001. It is possible that this difference may be the result of the changing coal composition. The overall Hg removal efficiency across the venturi scrubber was essentially the same in 2002 and 2001: 93% and 90%, respectively.

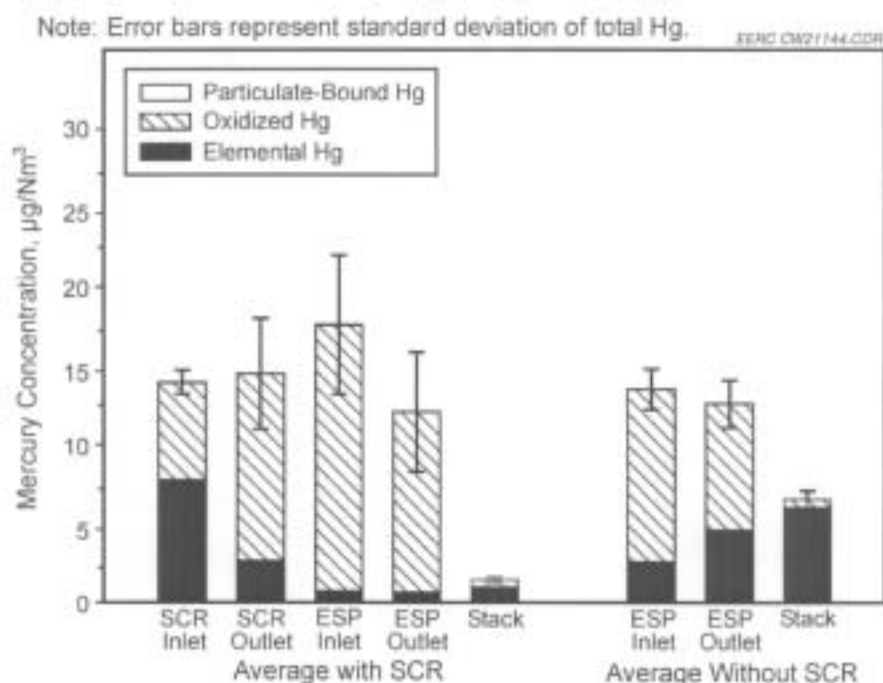
Figure ES-3 compares the OH Hg speciation results with SCR in operation and with SCR bypassed. At the air preheater outlet sampling location, 96% of the Hg is oxidized with SCR compared to 57% without SCR in service. In 2001, the comparison was 87% and 56%. As stated above, the overall Hg removal efficiency across the venturi scrubber was 93%; this is compared to only 44% when SCR was bypassed. This is supported by the Hg SCEM data that showed the average  $\text{Hg}^0$  concentration increasing from 1.1 to  $6.4 \mu\text{g}/\text{m}^3$  when SCR was bypassed.



**Figure ES-3**  
Comparisons of Mercury Speciation with the SCR in Service and with the SCR Bypassed at Site S4

### Site S5

The Hg results for Site S5 are summarized in Figure ES-4. As can be seen in Figure ES-4,  $\text{Hg}^{2+}$  increased from 44% to 81% across the SCR catalyst and was 95% at the ESP inlet sampling location. For the unit without SCR, the percentage of  $\text{Hg}^{2+}$  at the ESP inlet was 80%. The overall Hg removal efficiency across the ESP and wet FGD was 90% for the unit with SCR. This is compared to 51% for the unit without SCR. It should be noted that the results for the unit without SCR showed an increase in  $\text{Hg}^0$  ( $4.7$  to  $6.1 \mu\text{g}/\text{Nm}^3$ ) across the wet FGD. The increase in  $\text{Hg}^0$  was considerably less ( $0.7$  to  $1.0 \mu\text{g}/\text{Nm}^3$ ) for the unit with SCR.

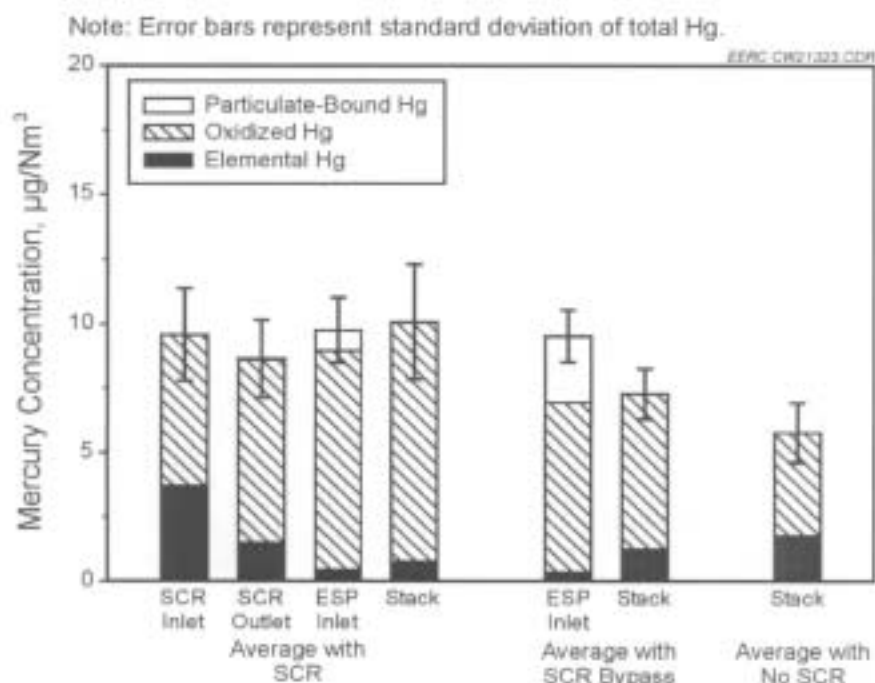


**Figure ES-4**  
**Mercury Speciation Results Compared for a Unit with SCR and Without SCR at Site S5**

### Site S6

The results of flue gas testing from S6 are summarized in Figure ES-5.  $\text{Hg}^{2+}$  increased from 64% to 83% across the SCR catalyst and was 87% at the ESP inlet sampling location. For the unit with SCR bypassed, the percentage of  $\text{Hg}^{2+}$  at the ESP inlet was 69%. However, as shown in Figure ES-5, there appeared to be more particulate-bound Hg measured when SCR was bypassed.

The test at Site S6 was conducted to evaluate the impact of SCR on Hg speciation when a low-sulfur compliance coal was fired; therefore, there was no wet FGD system on either test unit. Within the variation of the data, the presence of SCR had no apparent effect on Hg removal across the ESP (there was little if any for either case). Also, the Hg measured at the stacks had a high percentage of  $\text{Hg}^{2+}$ : 92% with SCR and 88% without SCR.



**Figure ES-5**  
**Mercury Speciation Results Comparing Units with and Without SCRs in Service at Site S6**

## Discussion of Overall Results

The primary goal of this project is to evaluate the effect SCR operation has on Hg speciation and, ultimately, on Hg emissions. The combined results from 2001 and 2002 testing are discussed below.

### *Effect of SCR on Mercury Speciation*

Table ES-3 presents the results of both the 2001 and 2002 testing. There is an increase in Hg oxidation across the SCR catalyst for those plants firing an eastern bituminous coal. However, the amount of oxidation that occurs across the catalyst is highly variable. It appears to be affected by coal properties as well as catalyst design and, possibly, catalyst age.

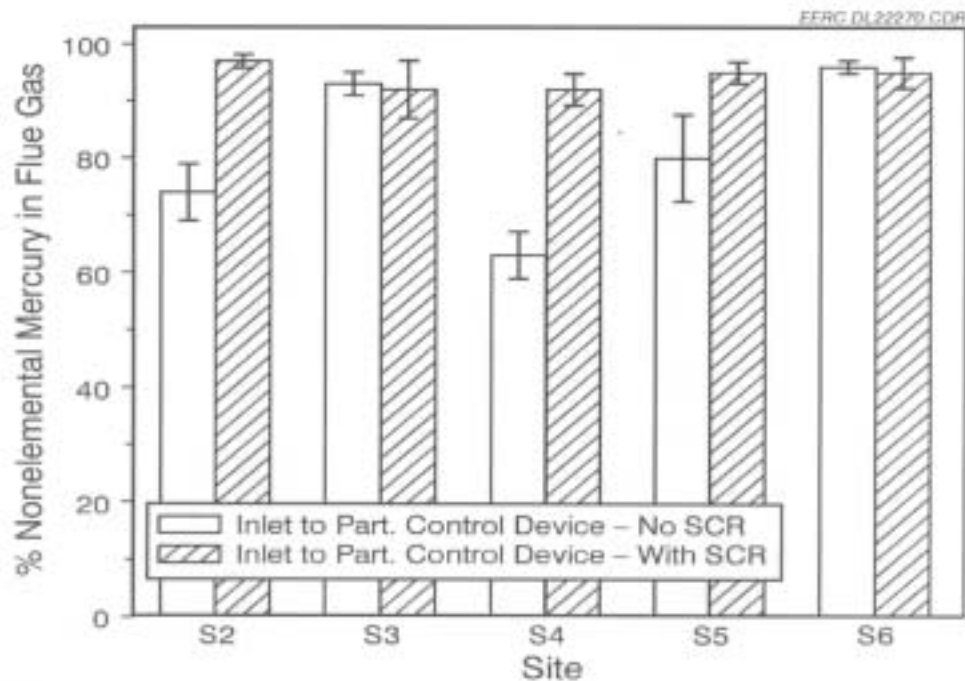
Although there is strong evidence that an SCR catalyst does promote Hg oxidation, to determine the overall effect of SCR, it was useful to conduct tests both with and without SCR in service at each site. Figure ES-6 shows the comparison. For three of the five sites, there is a higher concentration of nonelemental Hg ( $\text{Hg}^{2+}$  and particulate-bound Hg) when an SCR unit was present, based on measurements made at the inlet to the particulate control device. For the other two sites, S3 and S6, the percentage of nonelemental Hg was >90%, both with and without an SCR unit in service.

**Table ES-3**  
**Change in Mercury Oxidation across the SCR Catalyst**

Site	Year Sampled	SCR Inlet Hg <sup>2+</sup> , % of total Hg	SCR Outlet Hg <sup>2+</sup> , % of total Hg	Percentage Point Increase, <sup>a</sup> %
S1 <sup>b</sup>	2001	8	18	10
S2	2001	48	91	43
S2	2002	54	87	33
S3	2001	55	65	10
S4	2001	9	80	71
S4	2002	33	63	30
S5	2002	43	76	33
S6	2002	60	82	22

<sup>a</sup> Defined as (SCR Outlet % - SCR Inlet %).

<sup>b</sup> Site S1 fired a PRB coal; the others were eastern bituminous coals.



**Figure ES-6**  
**Mercury Concentrations at the Inlet of the Particulate Control Device with and Without the SCR, respectively**

### ***Effect of Catalyst Age on Mercury Speciation***

Data indicate that additional Hg oxidation can be expected if an SCR unit is installed on a unit firing an eastern bituminous coal. A potential concern is “Does the effectiveness of the Hg oxidation potential of SCR decrease with time?” As has been discussed previously, two of the facilities, S2 and S4, were tested in both 2001 and 2002 (both burned eastern bituminous coal). As Figures ES-1 and ES-2 show, there was a decrease in Hg oxidation across the SCR catalyst in 2002 as compared to 2001. However, the decrease in oxidation seen over time is less than that seen from coal variability. Additionally, it is expected that routine replacement of catalyst layers will minimize the effect. Also, mitigating circumstances at each plant prevent a definitive conclusion from being developed. At Site S2, the temperature of the SCR unit was ~10°F cooler due to humidification, and alkali was added upstream of the SCR unit. At both Sites S4 and S2, the coal chloride concentration was highly variable. Although there may be an “effect” of aging as measured across the SCR unit, Hg measurement at the inlet to the particulate control device indicates there was no significant difference at either site. To understand if these results are indicative of a catalyst aging effect, Hg speciation sampling is recommended at these plants for several additional years.

### ***Effect of the SCR on Wet FGD Performance for Mercury Control***

The underlying intent of understanding SCR-mediated Hg oxidation is to determine its potential to improve the Hg collection efficiency of existing ESPs, fabric filters and, in particular, FGD systems. In general, wet FGDs remove a large percentage (>90%) of  $\text{Hg}^{2+}$ . However, there has been evidence that some of the captured  $\text{Hg}^{2+}$  can be reduced in the wet FGD to  $\text{Hg}^0$  [10]. Although the sample set is very small (three facilities) and the wet FGDs tested to date are not representative of the most common FGD design in the United States (forced oxidation system), the data from this project indicate that some of the  $\text{Hg}^{2+}$  is chemically reduced to  $\text{Hg}^0$  in the wet FGD. This  $\text{Hg}^0$  passes through the FGD and is therefore not captured, resulting in an increase of  $\text{Hg}^0$  across the FGD. For the purposes of this report, this effect is termed reemission. As can be seen in Table ES-4, at all the sampling sites, there is an increase in  $\text{Hg}^0$  across the FGD. Also, the data seem to indicate the operation of the SCR unit ameliorates possible reemission.

**Table ES-4**  
**Effect of the SCR on Hg<sup>0</sup> Concentration Across the Wet FGDs**

Site	Year Sampled	FGD Inlet Hg <sup>0</sup> Conc., µg/Nm <sup>3</sup>	FGD Outlet Hg <sup>0</sup> Conc., µg/Nm <sup>3</sup>	Hg <sup>0</sup> Increase, <sup>a</sup> µg/Nm <sup>3</sup>	Total Hg Removal, %
<i>With SCR</i>					
S2	2001	0.4 <sup>b</sup>	0.9	0.5	89
S2	2002	0.3	1.3	1.0	84
S4	2001	0.5	0.8	0.3	90
S4	2002	1.0	1.3	0.3	91
S5	2002	0.7	1.0	0.3	91
<i>Without SCR</i>					
S2	2001	3.4 <sup>2</sup>	5.0	1.6	51
S4	2001	5.6	7.1	1.5	46
S4	2002	5.7	8.0	2.3	44
S5	2002	4.7	6.1	1.4	51

<sup>a</sup> Defined as (FGD outlet Hg<sup>0</sup> conc. - FGD inlet Hg<sup>0</sup> conc.).

<sup>b</sup> For 2001 Site S2 data, the ESP inlet data were used because the FGD inlet Hg concentration values appear to be clear outliers.

## Summary

The primary conclusions based on the test results are:

- For plants firing eastern bituminous coals, Hg<sup>0</sup> can be oxidized across the SCR catalysts. The effect that SCR has on Hg speciation (i.e., extent of additional oxidation that occurs) may be dependent upon the coal characteristics and catalyst properties. The percentage increase of Hg<sup>2+</sup> at the SCR outlet ranged from 10% at Site S3 to 71% at Site S4.
- At both sites where sampling was done in 2001 and 2002, there appeared to be a decrease in Hg oxidation across the SCR catalyst with time. However, at both facilities, the decrease was minimal, and other possible explanations related to changes in the plant's operation might explain the decrease. These changes do not allow a definitive conclusion to be reached concerning the effect of catalyst age (an additional ozone season) on SCR/Hg oxidation. It is important to note that the measured Hg oxidation at the inlet to the particulate control device was the same (within the variability of the data) for both years.
- Based on the limited data at three plants (five total data sets), SCR operation may reduce the extent of reemission across the wet FGDs. For the tests with SCR in service, the increase appears to be very small and is generally within the variability of the data. Nevertheless, five data points show an increase in Hg<sup>0</sup>. When SCR is not in service, it appears that the reemission is more pronounced.



## Future Test Plans

Based on a review of these test results, several areas will require further investigation. DOE, EPA, and EPRI are planning to conduct additional full-scale, as well as bench- and pilot-scale, studies to address the following:

- The effect of SCR for a PRB pulverized coal application.
- The effect of FGDs on Hg capture, in particular Hg reemission.
- The effect of SCR when PRB-bituminous-blended coal is fired.
- The effect of catalyst age on Hg speciation.

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# CONTENTS

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<b>1 INTRODUCTION .....</b>	<b>1-1</b>
1.1 Potential Impacts of SCR on Mercury Speciation .....	1-1
1.2 Pilot-Scale Screening Tests Conducted at the EERC.....	1-2
1.3 2001 SCR Mercury Field-Sampling Project .....	1-3
1.4 Project Goals and Objectives .....	1-5
1.5 Sampling Approach.....	1-5
1.5.1 Mercury Sampling Using the Ontario Hydro Mercury Speciation Method.....	1-5
1.5.2 Mercury Sampling Using Hg SCEMs .....	1-6
1.5.3 Other Flue Gas Analyses .....	1-7
1.5.4 Mass Balance.....	1-7
1.5.5 Plant Operation Data .....	1-7
<b>2 SITE S2 .....</b>	<b>2-1</b>
2.1 Site Description and Configuration .....	2-1
2.2 Sampling Approach.....	2-2
2.2.1 Flue Gas Sample Streams.....	2-3
2.2.2 Other Sample Streams .....	2-3
2.3 Process Operating Conditions.....	2-4
2.4 Sampling Results .....	2-7
2.4.1 OH Flue Gas Mercury Results.....	2-7
2.4.2 Hg SCEM Results .....	2-8
2.4.3 Coal Analysis Results.....	2-11
2.4.4 ESP Ash and FGD Mercury Results .....	2-12
2.4.5 NH <sub>3</sub> Slip and SO <sub>3</sub> Flue Gas Results .....	2-13
2.5 Mercury Mass Balance.....	2-14
2.6 General Observations from S2.....	2-14
<b>3 SITE S4 .....</b>	<b>3-1</b>

3.1	Site Description and Configuration .....	3-1
3.2	Sampling Approach.....	3-2
3.2.1	Flue Gas Sample Streams.....	3-3
3.2.2	Other Sample Streams .....	3-3
3.3	Process Operating Conditions.....	3-3
3.4	Sampling Results .....	3-5
3.4.1	OH Flue Gas Mercury Results.....	3-5
3.4.2	Hg SCEM Results .....	3-7
3.4.3	Coal Analysis Results.....	3-9
3.4.4	Mercury Collected by the Venturi Scrubber .....	3-10
3.4.5	NH <sub>3</sub> Slip and SO <sub>3</sub> Flue Gas Results for Site S4 .....	3-11
3.5	Mercury Mass Balance.....	3-11
3.6	General Observations from S4.....	3-12
<b>4</b>	<b>SITE S5 .....</b>	<b>4-1</b>
4.1	Site Description and Configuration .....	4-1
4.2	Sampling Approach.....	4-3
4.2.1	Flue Gas Sample Streams.....	4-3
4.2.2	Other Sample Streams .....	4-4
4.3	Process Operating Conditions.....	4-4
4.4	Sampling Results .....	4-9
4.4.1	OH Flue Gas Mercury Results.....	4-9
4.4.2	Hg SCEM Results .....	4-11
4.4.3	Coal Analysis Results.....	4-14
4.4.4	ESP Ash Mercury Results .....	4-15
4.4.5	NH <sub>3</sub> Slip and SO <sub>3</sub> Flue Gas Results .....	4-16
4.5	Mercury Mass Balance.....	4-17
4.6	General Observations from S5.....	4-17
<b>5</b>	<b>SITE S6 .....</b>	<b>5-1</b>
5.1	Site Description and Configuration .....	5-1
5.2	Sampling Approach.....	5-4
5.2.1	Flue Gas Sample Streams.....	5-5
5.2.2	Other Sample Streams .....	5-5
5.2.3	Process Operating Conditions .....	5-6

5.3	Sampling Results .....	5-12
5.3.1	OH Flue Gas Mercury Results .....	5-12
5.3.2	Hg SCEM Results .....	5-14
5.3.4	Coal Analysis Results .....	5-20
5.3.5	ESP Ash Analysis .....	5-21
5.3.6	NH <sub>3</sub> Slip and SO <sub>3</sub> Flue Gas Results .....	5-21
5.4	Mercury Mass Balance .....	5-22
5.5	General Observations from S6 .....	5-23
<b>6</b>	<b>DISCUSSION OF OVERALL RESULTS .....</b>	<b>6-1</b>
6.1	The Change in Mercury Oxidation Across the SCR Catalysts .....	6-3
6.2	Effect of the SCR on Mercury Oxidation .....	6-5
6.3	Effect of SCR Catalyst Age on Mercury Speciation .....	6-6
6.4	SCR/Wet FGD Combination for Mercury Control .....	6-8
<b>7</b>	<b>CONCLUSIONS .....</b>	<b>7-1</b>
	Future Test Plans .....	7-1
<b>8</b>	<b>QUALITY ASSURANCE/QUALITY CONTROL .....</b>	<b>8-1</b>
8.1	Process Data Evaluation .....	8-1
8.2	Sampling Quality Control Evaluation .....	8-2
8.3	Evaluation of Measurement Data Quality .....	8-3
8.4	OH Method Error Analysis .....	8-5
<b>9</b>	<b>REFERENCES .....</b>	<b>9-1</b>
<b>A</b>	<b>SAMPLING METHODS AND PROCEDURES .....</b>	<b>A-1</b>
	Ontario Hydro Mercury Speciation Method (OH method) .....	A-1
	Continuous Mercury Monitors .....	A-4
	Atomic Fluorescence-Based Hg SCEMs .....	A-4
	Atomic Absorption-Based Hg SCEMs .....	A-4
	Flue Gas Pretreatment/Conversion .....	A-5
	Auxiliary Flue Gas Measurements .....	A-6
	O <sub>2</sub> Determination .....	A-6
	CO <sub>2</sub> Determination .....	A-6
	Chlorides, NH <sub>3</sub> , and SO <sub>3</sub> .....	A-6

Reference .....	A-7
<b>B MERCURY MEASUREMENTS .....</b>	<b>B-1</b>
B.1 Mercury Measurements Made at Site S2 .....	B-1
Complete OH Data Set .....	B-1
Coal Mercury and Chloride Analyses .....	B-2
B.2 Mercury Measurements Made at Site S4 .....	B-3
Complete OH Data Set .....	B-3
B.3 Mercury Measurements Made at Site S5 .....	B-5
Complete OH Data Set .....	B-5
B.4 Mercury Measurements Made at Site S6 .....	B-8
Complete OH Data Set .....	B-8
<b>C COMPLETE AUXILIARY FLUE GAS DATA FOR ALL SITES .....</b>	<b>C-1</b>
<b>D QUALITY ASSURANCE/QUALITY CONTROL .....</b>	<b>D-1</b>
Ontario Hydro (OH) Method .....	D-1
Instrument Setup and Calibration .....	D-1
Presampling Preparation .....	D-2
Glassware and Plasticware Cleaning and Storage .....	D-2
Analytical Reagents .....	D-2
Blanks and Spikes .....	D-2
QA/QC Checks for Data Reduction and Validation .....	D-9
Data Reduction .....	D-9
Data Validation .....	D-9
Sample Identification and Chain of Custody .....	D-9
Personnel Responsibilities and Test Schedule .....	D-9
Test Site Organization .....	D-9
Test Preparations .....	D-10
Construction of Special Sampling Equipment and Modifications to the Facility .....	D-10
General Services Provided by the Facility .....	D-10
Access to Sampling Sites .....	D-10
Sample Recovery Areas .....	D-10
Test Personnel Responsibilities and Detailed Schedule .....	D-10
<b>E SAMPLE CALCULATIONS .....</b>	<b>E-1</b>

Volume of Gas Sample .....	E-1
Volume of Water Vapor .....	E-1
Water Vapor in the Gas Stream.....	E-2
Dry Molecular Weight.....	E-2
Molecular Weight .....	E-2
Average Stack Gas Velocity .....	E-2
Isokinetic Sampling Rate.....	E-3
Volume of Gas Sample Corrected to 3% O <sub>2</sub> .....	E-4
Mercury .....	E-4
F <sub>d</sub> .....	E-4





## LIST OF FIGURES

Figure 2-1 Schematic of Site S2 Showing Sample Locations from Horizontal and Vertical Perspectives .....	2-2
Figure 2-2 Plant Operation Data for Site S2 .....	2-5
Figure 2-3 Comparison of Mercury Speciation Results 2001 and 2002 for Site S2 .....	2-8
Figure 2-4 Hg SCCEM Results for Site S2 .....	2-10
Figure 2-5 Average $Hg^{2+}$ as Measured by Hg SCCEMs (total Hg - $Hg^0$ ) for Site S2 .....	2-11
Figure 3-1 Schematic of Site S4 Showing Sample Locations from a Vertical and Horizontal Perspective .....	3-2
Figure 3-2 Plant Operation Data for Site S4 .....	3-4
Figure 3-3 Comparison of Mercury Speciation Results with the SCR in Service and with the SCR Bypassed .....	3-6
Figure 3-4 Comparison of Mercury Speciation Results 2001 and 2002 for Site S4 .....	3-7
Figure 3-5 Hg SCCEM Results for Site S4 .....	3-8
Figure 3-6 Average $Hg^{2+}$ as Measured by Hg SCCEMs (Total Hg - $Hg^0$ ) for Site S4 .....	3-9
Figure 4-1 Schematic of Site S5 Showing Sample Locations for the Unit with the SCR from a Vertical and Horizontal Perspective .....	4-2
Figure 4-2 Schematic of Site S5 Showing Sample Locations for the Unit with No SCR from a Vertical and Horizontal Perspective .....	4-3
Figure 4-3 Plant Operation Data for Site S5 for the Unit with the SCR .....	4-5
Figure 4-4 Plant Operation Data for Site S5 for the Unit with No SCR .....	4-7
Figure 4-5 Comparison of Mercury Speciation Results with the SCR and Without an SCR at Site S5 .....	4-11
Figure 4-6 Hg SCCEM Results for Site S5 for the Unit with an SCR .....	4-12
Figure 4-7 Hg SCCEM Results for Site S5 for the Unit with No SCR .....	4-13
Figure 5-1 Schematic of Site S6 Showing Sample Locations for Unit 1 with the SCR in Service from a Vertical and Horizontal Perspective .....	5-2
Figure 5-2 Schematic of Site S6 Showing Sample Locations for Unit 2 with the SCR Bypassed from a Vertical and Horizontal Perspective .....	5-3
Figure 5-3 Schematic of Site S6 Showing Sample Locations for Unit 4 with No SCR from a Vertical and Horizontal Perspective .....	5-4
Figure 5-4 Plant Operation Data for Site S6 for Unit 1 with the SCR in Service .....	5-7
Figure 5-5 Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed .....	5-9
Figure 5-6 Plant Operation Data for Site S5 for Unit 4 with No SCR .....	5-11
Figure 5-7 Comparison of Mercury Speciation Results for the Three Test Units .....	5-13

Figure 5-8 Hg SCCEM Results for Site S6 for Unit 1 with the SCR in Service .....	5-15
Figure 5-9 Hg SCCEM Results for Site S6 for Unit 2 with the SCR Bypassed .....	5-16
Figure 5-10 Hg SCCEM Results for Site S6 for Unit 4 with No SCR .....	5-17
Figure 5-11 Average $Hg^{2+}$ as Measured by Hg SCCEMs (total Hg - $Hg^0$ ) for Site S6 Unit 1 (SCR on-line) .....	5-18
Figure 5-12 Average $Hg^{2+}$ as Measured by Hg SCCEMs (total Hg - $Hg^0$ ) for Site S6 Unit 2 (SCR bypassed) .....	5-19
Figure 5-13 Hg SCCEM Results for Site S6 for Unit 2 with SCR Bypassed .....	5-19
Figure 6-1 Percent of Oxidized $Hg^{2+}$ at the Inlet of the SCR System as a Function of Chloride Content of the Coal .....	6-4
Figure 6-2 Mercury Speciation Results Comparing All the Sites Tested Firing Eastern Bituminous Coal .....	6-5
Figure 6-3 Comparison of Mercury Speciation Results from 2001 and 2002 at Site S2 .....	6-7
Figure 6-4 Comparison of Mercury Speciation Results from 2001 and 2002 at Site S4 .....	6-7
Figure A-1 Schematic of the OH Mercury Speciation Train .....	A-1
Figure A-2 Sample Recovery Scheme for the OH Mercury Speciation Train .....	A-3
Figure A-3 Schematic of the EERC Pretreatment/Conversion System for Use with Hg SCCEMs .....	A-5

## LIST OF TABLES

Table 1-1 Summary of Plant Configuration from 2001 Test Program .....	1-4
Table 2-1 Sampling Test Matrix for Site S2 .....	2-3
Table 2-2 Average Auxiliary Flue Gas Data for Site S2 .....	2-7
Table 2-3 OH Average and Percentage of Total Mercury Results for S2 .....	2-7
Table 2-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S2 .....	2-11
Table 2-5 Coal Analysis for Site S2 .....	2-12
Table 2-6 Analysis of ESP Hopper Ash and FGD Material for Site S2 .....	2-13
Table 2-7 NH <sub>3</sub> Slip and SO <sub>3</sub> Results at Site S2 .....	2-13
Table 3-1 Sampling Test Matrix for Site S4 .....	3-3
Table 3-2 Average Auxiliary Flue Gas Data for Site S4 .....	3-5
Table 3-3 Average OH Mercury and Results for Site S4 .....	3-6
Table 3-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S4 .....	3-9
Table 3-5 Coal Analysis for Site S4 .....	3-10
Table 3-6 Partitioning of Mercury in Material Collected from Venturi Scrubber .....	3-11
Table 3-7 S4 Flue Gas, NH <sub>3</sub> Slip, and SO <sub>3</sub> Results for Site S4 .....	3-11
Table 3-8 Average Mercury Emission Factors for Site S4 .....	3-12
Table 4-1 Sampling Test Matrix for Site S5 .....	4-4
Table 4-2 Auxiliary Flue Gas Data for Site S5 .....	4-9
Table 4-3 Average and Percentage of Total OH Mercury Results for S5 .....	4-10
Table 4-4 Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg SCEM Data for Site S5 .....	4-14
Table 4-5 Coal Analysis for Site S5 .....	4-15
Table 4-6 Analysis of ESP Hopper Ash .....	4-16
Table 4-7 Flue Gas SO <sub>3</sub> and NH <sub>3</sub> Results for Site S5 .....	4-16
Table 4-8 Average Mercury Emission Factors for Site S5 .....	4-17
Table 5-1 Specifications of Site S6 Units .....	5-1
Table 5-2 Sampling Test Matrix for Site S6 .....	5-5
Table 5-3 Auxiliary Flue Gas Data for Site S6 .....	5-12
Table 5-4 Average and Percentage of Total OH Mercury Results for S6 .....	5-13
Table 5-5 Statistical Variation of the Mercury Results Based on the Hg SCEM Data for Site S6 .....	5-18

Table 5-6 Coal Analysis for Site S6.....	5-20
Table 5-7 Analysis of ESP Hopper Ash.....	5-21
Table 5-8 Flue Gas SO <sub>3</sub> and NH <sub>3</sub> Results for Site S6 .....	5-22
Table 5-9 Average Mercury Emission Factors for Site S6 .....	5-22
Table 6-1 Summary of SCR Program Plant Configuration.....	6-2
Table 6-2 Average Analysis of Coals Fired During 2001 and 2002 Field Tests .....	6-3
Table 6-3 Change in Mercury Oxidation Across the SCR Catalyst .....	6-4
Table 6-4 Net Change in Hg <sup>2+</sup> as Measured at the Inlet to the Particulate Control Device.....	6-6
Table 6-5 Effect of the SCR on Hg <sup>0</sup> Concentration Across the Wet FGDs.....	6-8
Table 8-1 Elements of the QA/QC Plan.....	8-4
Table A-1 Sample Train Components for the OH Method .....	A-2
Table B-1 OH Mercury Data for Site S2 with the SCR in Service .....	B-1
Table B-2 Coal Analysis Completed at Site S2 .....	B-2
Table B-3 OH Mercury Data for Site S4 with the SCR In Service .....	B-3
Table B-4 OH Mercury Data for Site S4 with the SCR Bypassed .....	B-4
Table B-5 OH Mercury Data for Site S5 for Unit with the SCR .....	B-5
Table B-6 OH Mercury Data for Site S5 for Unit Without an SCR.....	B-6
Table B-7 Coal Mercury and Chloride Analyses.....	B-7
Table B-8 OH Mercury Data for Site S6 for Unit 1 (SCR) .....	B-8
Table B-9 OH Mercury Data for Site S6 for Unit 2 (SCR bypassed) .....	B-9
Table B-10 OH Mercury Data for Site S6 for Unit 4 (no SCR) .....	B-10
Table B-11 Coal Mercury and Chloride Analyses for Site S6 .....	B-10
Table C-1 Auxiliary Flue Gas Data for Site S2 with SCR in Service .....	C-1
Table C-2 Auxiliary Flue Gas Data for Site S4 with SCR in Service .....	C-2
Table C-3 Auxiliary Flue Gas Data for Site S4 with SCR Bypassed .....	C-3
Table C-4 Auxiliary Flue Gas Data for Site S5 for the Unit with an SCR.....	C-4
Table C-5 Auxiliary Flue Gas Data for Site S5 for the Unit Without an SCR.....	C-5
Table C-6 Auxiliary Flue Gas Data for Site S6 for Unit 1 (SCR) .....	C-6
Table C-7 Auxiliary Flue Gas Data for Site S6 for Unit 2 (SCR bypassed) .....	C-7
Table C-8 Auxiliary Flue Gas Data for Site S6 for Unit 4 (no SCR) .....	C-8
Table D-1 Results of Mercury Speciation Field Blanks at Site S2.....	D-3
Table D-2 Results of Mercury Speciation Field Spikes at Site S2.....	D-4
Table D-3 Results of Mercury Speciation Field Spikes at Site S4.....	D-5
Table D-4 Results of Mercury Speciation Field Blanks at Site S5.....	D-5
Table D-5 Results of Mercury Speciation Field Spikes at Site S5.....	D-6
Table D-6 Results of Mercury Speciation Field Blanks at Site S6.....	D-7
Table D-7 Results of Mercury Speciation Field Spikes at Site S6.....	D-8
Table D-8 Key Project Personnel.....	D-11

Table D-9 Test Personnel and Responsibilities.....	D-12
Table D-10 Typical Test Schedule for a 4-Week Project .....	D-13



# 1

## INTRODUCTION

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Coal combustion by electric utilities is a large source of anthropogenic mercury (Hg) emissions in the United States, according to the most recent data, accounting for 45 tons/yr of total point source Hg emissions [1]. In December 2000, the U.S. Environmental Protection Agency (EPA) issued an intent to regulate Hg from coal-fired utility boilers [2]. As a result, many utilities have become proactive in evaluating the effectiveness of current air pollution control technologies, as well as new technologies for Hg control [1,3–5].

Hg emissions from coal-fired boilers can be empirically classified, based on the capabilities of currently available analytical methods, into three main forms: elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ), and particulate-bound Hg. Particulate-associated Hg ( $\text{Hg}_p$ ) can be removed from flue gas by conventional air pollution control devices such as an electrostatic precipitator (ESP) or a baghouse.  $\text{Hg}^{2+}$  compounds are readily captured in flue gas desulfurization (FGD) units.  $\text{Hg}^0$  is most likely to escape air pollution control devices and be emitted to the atmosphere. Total Hg concentrations in coal combustion flue gas typically range from 3 to 15  $\mu\text{g}/\text{Nm}^3$ ; however,  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and particulate-bound Hg concentrations are quite variable depending on coal composition and combustion conditions [6].

In addition to Hg, coal-burning power plants are a significant anthropogenic source of nitrogen oxide ( $\text{NO}_x$ ) emissions to the atmosphere.  $\text{NO}_x$  emissions are an environmental concern primarily because they are associated with increased acidic precipitation, as well as fine-particle and ozone formation. Depending on the size and type of boiler, the 1990 Clean Air Act Amendments require specific reductions in  $\text{NO}_x$  emissions from coal-fired electric utilities. The most common  $\text{NO}_x$  reduction strategy is the installation of low- $\text{NO}_x$  burners. These burners have the capability of reducing  $\text{NO}_x$  emissions by 40%–60%. However, with possible establishment of fine particulate ( $\text{PM}_{2.5}$ ), regional haze, ozone regulations, and  $\text{NO}_x$  state implementation plans, there is increased incentive to reduce  $\text{NO}_x$  emissions to a level below what can be achieved using low- $\text{NO}_x$  burners. Selective catalytic reduction (SCR) technology, which can reduce  $\text{NO}_x$  emissions by >90%, is, therefore, becoming more attractive, particularly because catalyst costs continue to decrease and the knowledge base for using SCR reactors is expanding. It is planned that approximately 100 gigawatts of coal-fired electrical capacity will have SCRs installed by 2005 [7].

### 1.1 Potential Impacts of SCR on Mercury Speciation

SCR units achieve lower  $\text{NO}_x$  emissions by catalytically reducing  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$  in the presence of ammonia ( $\text{NH}_3$ ). The catalysts used in SCR units are generally metal oxides such as titanium dioxide ( $\text{TiO}_2$ )-supported vanadium oxide ( $\text{V}_2\text{O}_5$ ). These units are generally operated at



about 650°–750°F (343°–399°C). Initial laboratory-scale testing indicated that metal oxides, including  $V_2O_5$  and  $TiO_2$ , promoted the conversion of  $Hg^0$  to  $Hg^{2+}$  or particulate-bound Hg in relatively simple flue gas mixtures [8]. In addition, pilot- and full-scale Hg speciation measurements in European and U.S. coal-fired boilers equipped with SCR reactors have shown the potential to promote the formation of  $Hg^{2+}$  [9–11]. Therefore, it was hypothesized that the use of SCR may improve the Hg-control efficiency of existing air pollution control devices by promoting  $Hg^{2+}$  or particulate-bound Hg formation.

Possible mechanisms by which SCR operation could affect Hg speciation include:

- Catalytic oxidation of the Hg. Evidence indicates that vanadium-based catalysts can promote the formation of  $Hg^{2+}$  [9–12].
- Changing the flue gas chemistry. The significant reduction in flue gas  $NO_x$  and slight increase in  $NH_3$  concentrations associated with SCR may affect Hg speciation. It is well known that  $NO_x$ , particularly  $NO_2$ , has a substantial effect on Hg speciation [13]. The gas-phase effects of  $NH_3$  on Hg are unknown. SCR units also have the potential to catalyze the formation of sulfur trioxide ( $SO_3$ ) and, potentially, chlorine ( $Cl_2$ ), which may then react with Hg [14–18].
- The SCR unit provides additional residence time for the oxidation of Hg to take place.
- Changing the fly ash chemical composition. It is possible that SCR operation may change the surface chemistry of the fly ash particles such that their ability to adsorb or convert Hg species is altered.
- Increasing wall deposition. SCR systems may result in the deposition of ammonium bisulfate and ammonium sulfate in the air preheater and duct walls. It is unknown whether increased deposition could impact Hg emissions or speciation.

## **1.2 Pilot-Scale Screening Tests Conducted at the EERC**

To investigate the effects of SCR on Hg speciation in a coal combustion system, EPRI, the U.S. Department of Energy (DOE), and EPA funded a pilot-scale project at the Energy & Environmental Research Center (EERC) [10]. The primary objective for the pilot-scale tests was to determine whether  $NH_3$  injection or the catalyst in a representative SCR system promote the conversion of  $Hg^0$  to  $Hg^{2+}$  or particulate-bound Hg. Although this project was a screening evaluation and not a complete parametric study, it was designed to evaluate potential mechanisms for Hg conversion and the various coal parameters (like chemical composition) that may affect the degree of conversion.

Three bituminous coals and a Powder River Basin (PRB) subbituminous coal were burned in a pilot-scale combustion system equipped with an  $NH_3$  injection system, SCR reactor, and ESP. The selection criteria for the four coals investigated were the significant differences in their sulfur and chloride contents.

The results from the tests indicated that  $NH_3$  injection and, possibly, the SCR catalyst promote the conversion of  $Hg^{2+}$  to particulate-bound Hg in the coal combustion flue gases for two of the

bituminous coals, but this was not the case for the PRB coal. The results were inconclusive for the third bituminous coal. When the limited data are used in a linear regression analysis, it appears that the chloride, sulfur, and calcium contents of the coal correlate with Hg speciation across the SCR unit. Because of the inherent concerns related to small pilot-scale tests (surface area-to-volume ratios, different flue gas chemistries, and time and temperature profiles), it was decided that sampling at full-scale power plants was necessary. Therefore, beginning in 2001, EPRI, DOE, and EPA funded projects with the EERC and others to conduct Hg sampling at power plants with SCR technology.

### 1.3 2001 SCR Mercury Field-Sampling Project

The test program for 2001 was developed to address the limitations of pilot-scale testing by applying information obtained from previous work to several full-scale electric-generating facilities. A summary of plants and their configuration is provided in Table 1-1. The overall objective of 2001 testing was to evaluate the effects of SCR operation, selective noncatalytic reduction (SNCR), and flue gas conditioning on speciated Hg emissions at full-scale plants. More specifically, the objective was to evaluate Hg speciation across the unit as a result of these technologies. The results of testing conducted for the 2001 program are summarized below and can be found in "Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury" [11].

In general, data from 2001 testing indicated that SCR has the potential to increase Hg oxidation. However, significant differences in Hg speciation were observed between plants even with similar coal classifications. The possible reasons for these disparate differences likely include a combination of the following:

- Coal chloride concentration – The chloride level in the coal is the most straightforward approach to estimating Cl (HCl and Cl<sub>2</sub>) in flue gas, although it is possible that alkalinity in the fly ash may tie up Cl and reduce its availability for some coals.
- Inlet percentage of Hg<sup>2+</sup> – For plants with a high proportion of the inlet Hg already oxidized, the potential increase is much lower.
- Other flue gas constituents (e.g., alkalinity, SO<sub>2</sub>, and SO<sub>3</sub>).
- SCR system/catalyst properties – e.g., space velocity, area velocity, catalyst type, catalyst age, or number of catalyst layers.

It was thus theorized that the Hg speciation and associated oxidation of Hg across the SCR is highly dependent upon coal characteristics.

The primary conclusions from this effort were:

- At all four sites tested with SCR, an increase in Hg oxidation was observed across the SCR unit. It varied from 10% at Sites S1 and S3 to 71% at Site S4. SCR units can assist in converting Hg<sup>0</sup> to Hg<sup>2+</sup>; however, the effect appears to be coal-specific and, possibly, catalyst-specific.

**Table 1-1**  
**Summary of Plant Configuration from 2001 Test Program**

Site	Coal	Boiler Type	Boiler Size, MW	Low-NO <sub>x</sub> Burners	Catalyst Vendor and Type	Catalyst Age	SCR Space Velocity, hr <sup>-1</sup>	Particulate Control	Sulfur Control
S1	PRB subbit.	Cyclone	650	No	Cornmetech honeycomb	2 ozone seasons	1800	ESP	None
S2	OH bit.	Wall-fired	1300	Yes	Siemens/ Westinghouse plate	3 months	2125	ESP	Wet FGD <sup>a</sup>
S3	PA bit.	Tangential- fired	750	Yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	None
S4	KY bit.	Cyclone	650	No	Cornmetech honeycomb	1 ozone season	2275	Venturi scrubber	Venturi scrubber

<sup>a</sup> Flue gas desulfurization.

- For the two sites with SCR and wet FGD system (S2 and S4), a high percentage of the total Hg was removed, 89% and 90%, respectively. It should be noted that at Site S3 the percentage of  $\text{Hg}^{2+}$  at the outlet of ESP was 83%.
- Site S1 contained significant particulate-bound Hg, which was removed across the ESP, resulting in 85% total Hg removal. The high level of particulate-bound Hg may have been a result of the high carbon content of the ash (15% to 17%).
- Based on limited data (one site each), SNCR for  $\text{NO}_x$  control and  $\text{NH}_3$  flue gas conditioning for improving ESP performance appeared to have a fairly small effect on Hg oxidation.

Upon review of 2001 test results, it was evident that additional data would be necessary to quantify the effect SCR operation had on Hg oxidation, including the following:

- Determine the effect of firing a PRB in a more typical configuration
- Determine the effect of firing a low-sulfur compliance coal
- Determine the effect of catalyst aging
- Determine the effect of catalyst type and space velocity

In order to address these issues, the program was expanded, and additional testing was conducted in 2002. It should be noted that the highest priority given was to test a plant with SCR and a pulverized coal (pc)-fired PRB coal. Unfortunately, no plant could be identified for testing in 2002 with this configuration. However, plans are being made to test two PRB plants with SCR units in 2003 and 2004.

## 1.4 Project Goals and Objectives

The project goal is to determine the impact of SCR operation on Hg speciation and on Hg emissions. The specific objectives of the 2002 testing were to:

- Determine the change in Hg speciation across the SCR catalyst as a function of catalyst aging (an additional ozone season). Two plants that had been tested in 2001 were retested in 2002.
- Determine the effect of firing a compliance (low-sulfur) coal on Hg speciation across the SCR catalyst.
- Determine what effects SCR has on subsequent Hg speciation and the overall Hg removal for the particulate control device and, if present, the wet FGD.

## 1.5 Sampling Approach

### 1.5.1 Mercury Sampling Using the Ontario Hydro Mercury Speciation Method

At each facility, the overall sampling approach consisted of measuring Hg across each pollution control device (SCR, ESP, and wet FGD). In this way, the effect of these devices on Hg could be determined. To determine the overall effect of SCR on Hg speciation and subsequent removal,

sampling was done at a unit with SCR followed by testing either at a similar unit without SCR or with SCR bypassed. For example, if a plant had an SCR unit, ESP and wet FGD unit samples were taken at five locations as follows:

- SCR inlet
- SCR outlet (prior to the air heater)
- ESP inlet (downstream of the air heater)
- ESP outlet
- Wet FGD outlet (generally the stack)

In general, samples were taken in pairs across each device (i.e., inlet and outlet of the SCR) and in duplicate or triplicate.

The Ontario Hydro (OH) sampling was done using EPA Method 17, ensuring that the filter was at the same temperature as the flue gas. At the SCR inlet and outlet condition, the OH sample filter averaged between 600° and 750°F (316° and 399°C). Following the air heater, the flue gas temperature was between 250° and 350°F (121° and 177°C). Sampling was done at a single point rather than traversing the flue gas duct. For wet stack locations where the flue gas temperature was below 250°F (121°C), an external heater (Method 5 configuration) was used to maintain the filter temperature above 250°F (121°C).

Based on the OH data, for each plant the following were calculated:

- The change in Hg oxidation across the SCR unit. This is defined as the difference in the percent  $\text{Hg}^{2+}$  in the flue gas between the outlet and inlet of the SCR unit.
- Overall effect of SCR on Hg oxidation. This is defined as the difference in the percentage of  $\text{Hg}^{2+}$  at the inlet to the particulate control device with and without SCR.
- Overall Hg removal. This is defined as percentage based on the difference in total Hg measured at the inlet to the particulate control device and the stack.

### **1.5.2 Mercury Sampling Using Hg SCEMs**

Hg semicontinuous emission monitor (Hg SCEM) testing was done using the PS Analytical (PSA) or Tekran system with a stannous chloride (wet-chemistry) conversion system. Attempts were made to operate the Hg SCEMs at inlet and outlet locations; however, it was extremely difficult to maintain Hg SCEM operation on a continuous basis at locations upstream of particulate removal devices. Therefore, data from Hg SCEMs were collected primarily from ESP outlet or stack locations. Where applicable, OH data are compared to Hg SCEM data; however, in general, OH results with appropriate quality control (QC) provide a more defensible EPA-approved method of quantifying Hg concentration and emissions. The benefit or advantage of Hg SCEM operation is the real-time nature of the data. When operated continuously for several days, SCEMs provide valuable information on how Hg concentration and speciation changes with typical plant operation.

### **1.5.3 Other Flue Gas Analyses**

Other gases sampled for this project include  $\text{SO}_3$  and  $\text{NH}_3$  slip.  $\text{SO}_3$  was measured using the controlled condensation method, and  $\text{NH}_3$  slip was measured using Conditional Test Method 27. For most of the sites,  $\text{SO}_3$  was measured at the air preheater inlet (SCR outlet) and at the ESP inlet locations. The  $\text{NH}_3$  slip was measured at the air preheater inlet.

### **1.5.4 Mass Balance**

At each site coal, hopper ash and, where appropriate, FGD samples were collected and analyzed for Hg. These results, along with flue gas data, were used to quantitatively evaluate the fate of Hg throughout the unit.

### **1.5.5 Plant Operation Data**

Each plant provided operational information, such as plant load and flue gas CEM data, for the purposes of evaluating unit performance and flue gas chemistry. Differences existed between plants regarding the type, frequency, and form in which operational data existed. Therefore, the figures presenting these data are unique to each plant. Nevertheless, the information is useful for comparing Hg SCEM data with plant operational data and evaluating possible impacts on Hg speciation.



# 2

## SITE S2

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Site S2 was selected to provide data to determine the impact of catalyst aging on the potential of the SCR to oxidize Hg.

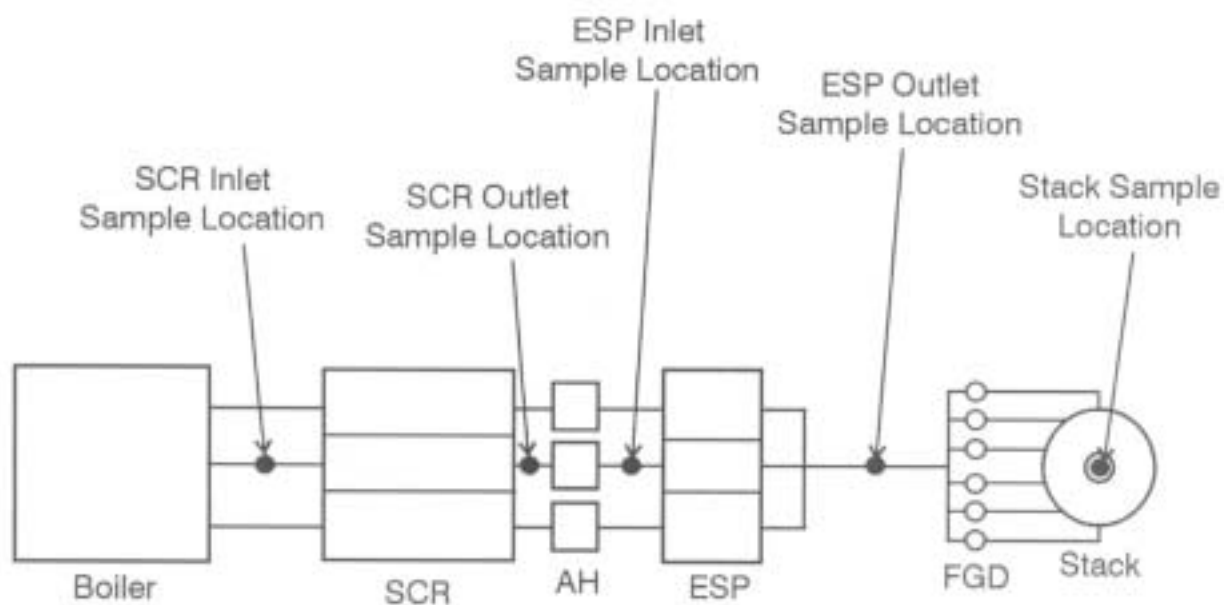
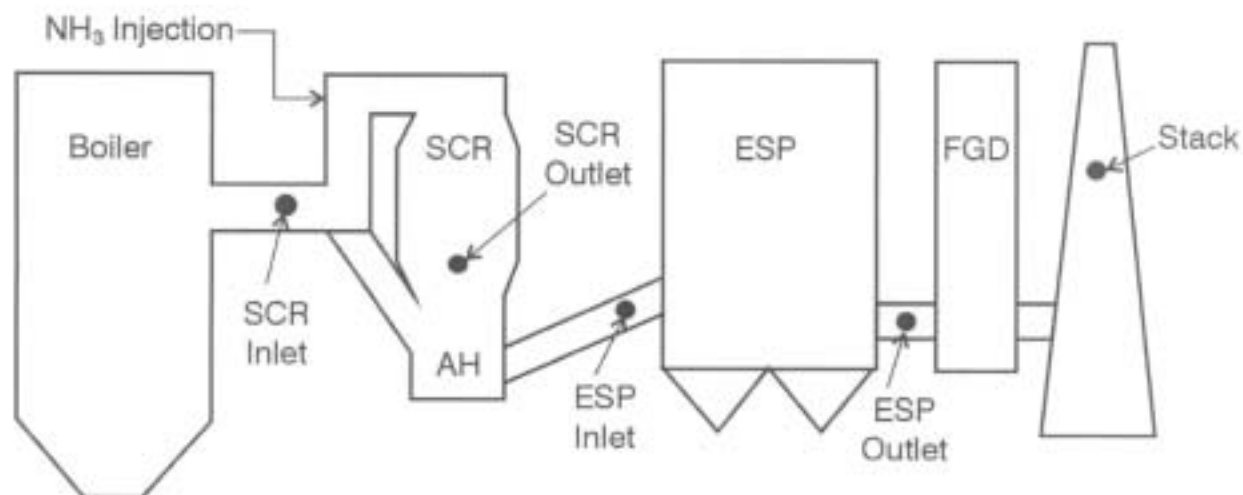
### 2.1 Site Description and Configuration

Site S2 fires a high-sulfur Ohio bituminous coal and employs SCR followed by an ESP and a wet FGD. The SCR unit at Site S2 utilizes a Siemens/Westinghouse plate catalyst with a space velocity of  $2125 \text{ hr}^{-1}$ . Although Site S2 had previously been tested in 2001, there were several operational differences in 2002. To control  $\text{SO}_3$  emission, alkali was injected just downstream of the boiler in 2002. Also, a humidification system had been installed upstream of the SCR unit to lower the SCR temperature  $\sim 10^\circ\text{F}$ . Finally, the coal may not have been from the same mine as that fired in 2001 as the Cl content in the coal was much less, 520 vs. 1330 ppm. The original intent at Site S2 was to operate 2 weeks with SCR in service and then, following the ozone season, bypass the SCR unit and test without SCR. However, as will be discussed later, there were operational problems at Site S2 that changed this test plan. General information about the configuration of the unit tested at Site 2 are found below:

- Fuel type: Ohio bituminous coal
- Boiler capacity: 1360 megawatts (MW)
- Boiler type: wall-fired
- $\text{NO}_x$  control: low- $\text{NO}_x$  burner and SCR
- Particulate control: ESP
- $\text{SO}_2$  control: magnesium-enhanced lime FGD

A schematic of Site S2 including sampling locations is shown in Figure 2-1.





**Figure 2-1**  
Schematic of Site S2 Showing Sample Locations from Horizontal and Vertical Perspectives

## 2.2 Sampling Approach

The sampling approach at S2 was similar to the previous year and is documented in *Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury* [11]. The objective of testing this unit again in 2002 was to evaluate the effect of catalyst aging on speciated Hg

emissions. As stated earlier, changes to the system, including using humidification to operate SCR at a lower temperature, make comparison and interpretation of 2001 and 2002 data difficult. Also, because of operational problems, the SCR unit was bypassed earlier than expected, and the complete test program was not able to be completed. However, Hg SCCEM data were collected for approximately 1 month: 2 weeks each with and without SCR on-line.

### 2.2.1 Flue Gas Sample Streams

Flue gas Hg speciation was measured at five locations using the OH method. Sample locations included the ESP inlet and outlet, SCR inlet and outlet, and stack. A test matrix is provided in Table 2-1. Where practical, OH measurements were conducted simultaneously across the ESP or FGD in an effort to quantify the effect each had on Hg concentration and speciation. In addition to Hg, flue gas samples were also taken to measure the total particulate loading, SO<sub>3</sub> concentrations, and NH<sub>3</sub> slip. The sampling methods used for all the sites are described in Appendix A.

**Table 2-1**  
**Sampling Test Matrix for Site S2<sup>a</sup>**

Date		SCR In	SCR Out	ESP In	Stack	SCR Out	SCR Out	ESP Out
Begin	End	OH	OH	OH	OH	SO <sub>3</sub>	NH <sub>3</sub>	NH <sub>3</sub>
07/16/02	07/20/02	3	3	2	2	3	2	2

<sup>a</sup> All samples were done with the SCR in service.

Longer-term Hg monitoring was planned using two Hg SCCEMs (Tekran): one located at the ESP inlet and the other at the ESP outlet. However, because of severe plugging of the inertial filter probe early in the test, both instruments were operated at the ESP outlet. One instrument measured total Hg and the other Hg<sup>0</sup>.

### 2.2.2 Other Sample Streams

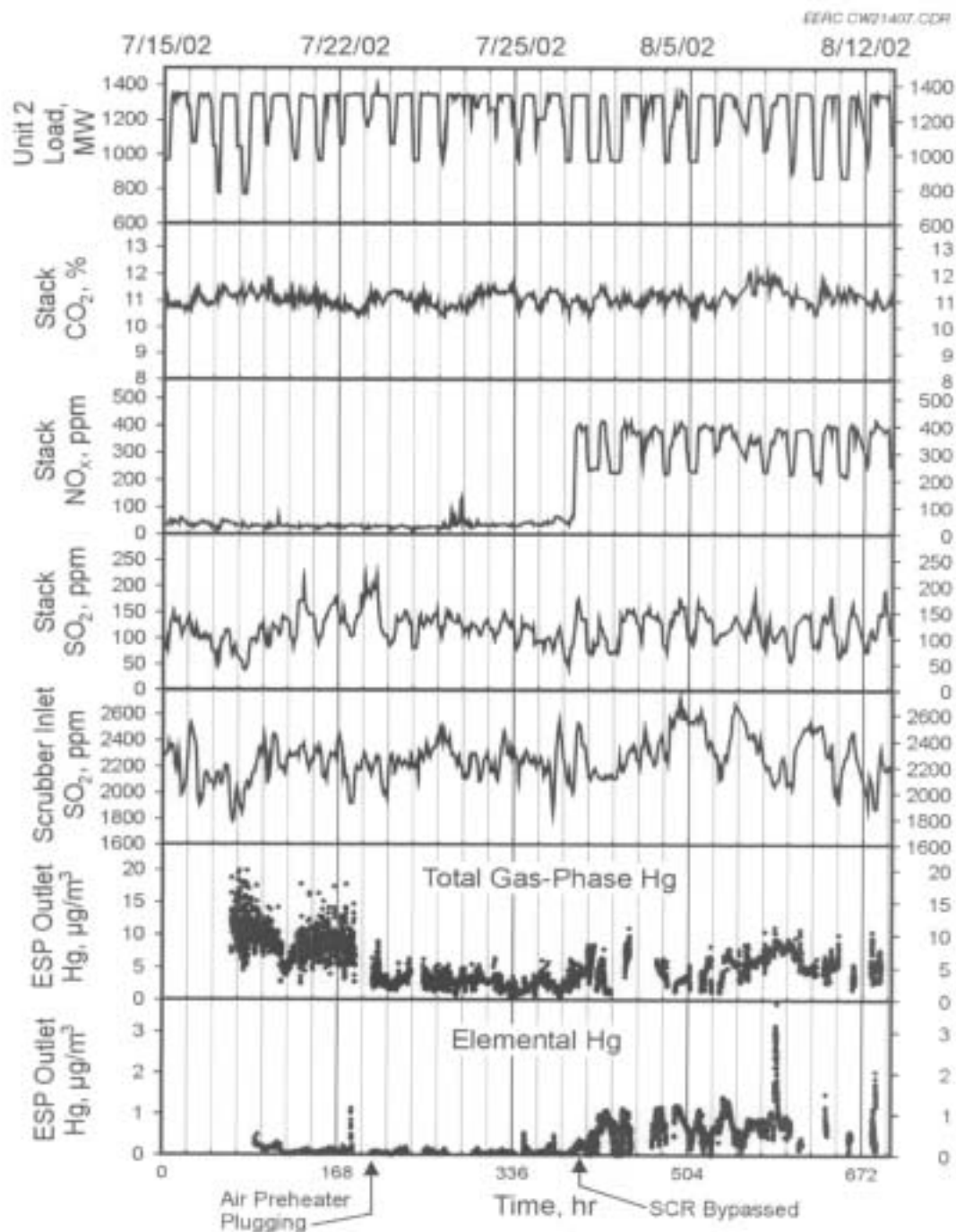
Samples of coal, fly ash, and FGD materials were collected in an effort to obtain representative operational data related to Hg speciation. These samples were analyzed for total Hg and, along with the flue gas emission data, were used to qualitatively evaluate the fate of Hg throughout the unit.

Coal samples and ESP hopper ash samples were collected each day of the test. The coal samples comprised coal from each coal mill that were pulled from the bunker and analyzed by the plant every 12 hours. The EERC received a split of these samples. The ESP hopper ash samples were taken as a field composite from the hoppers associated with the first field of both the upper and lower ESP. The FGD slurry samples were collected from the blowdown tank of the FGD.

## 2.3 Process Operating Conditions

Plant operational data are presented in Figure 2-2 for Site S2. The most significant change in plant operations is the bypassing of SCR. The amount of NO<sub>x</sub> coming out the stack increased significantly (from approximately 50 to 400 ppm) 390 hours into the test period after NH<sub>3</sub> injection was turned off and the SCR unit was bypassed. An increase in Hg<sup>0</sup> was observed with the Hg SCCEM and will be discussed later in this report. The average SO<sub>2</sub> collection efficiency of the FGD during the 4-week testing period was 95%, and the NO<sub>x</sub> removal efficiency of the SCR unit when in service was 90%.

Average auxiliary flue gas data including moisture, dust loading, and percent carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) were collected during the OH sampling from each sample location (Table 2-2). Values are within expected ranges (complete auxiliary flue gas data are provided in Appendix C, Table C-1).



**Figure 2-2**  
Plant Operation Data for Site S2

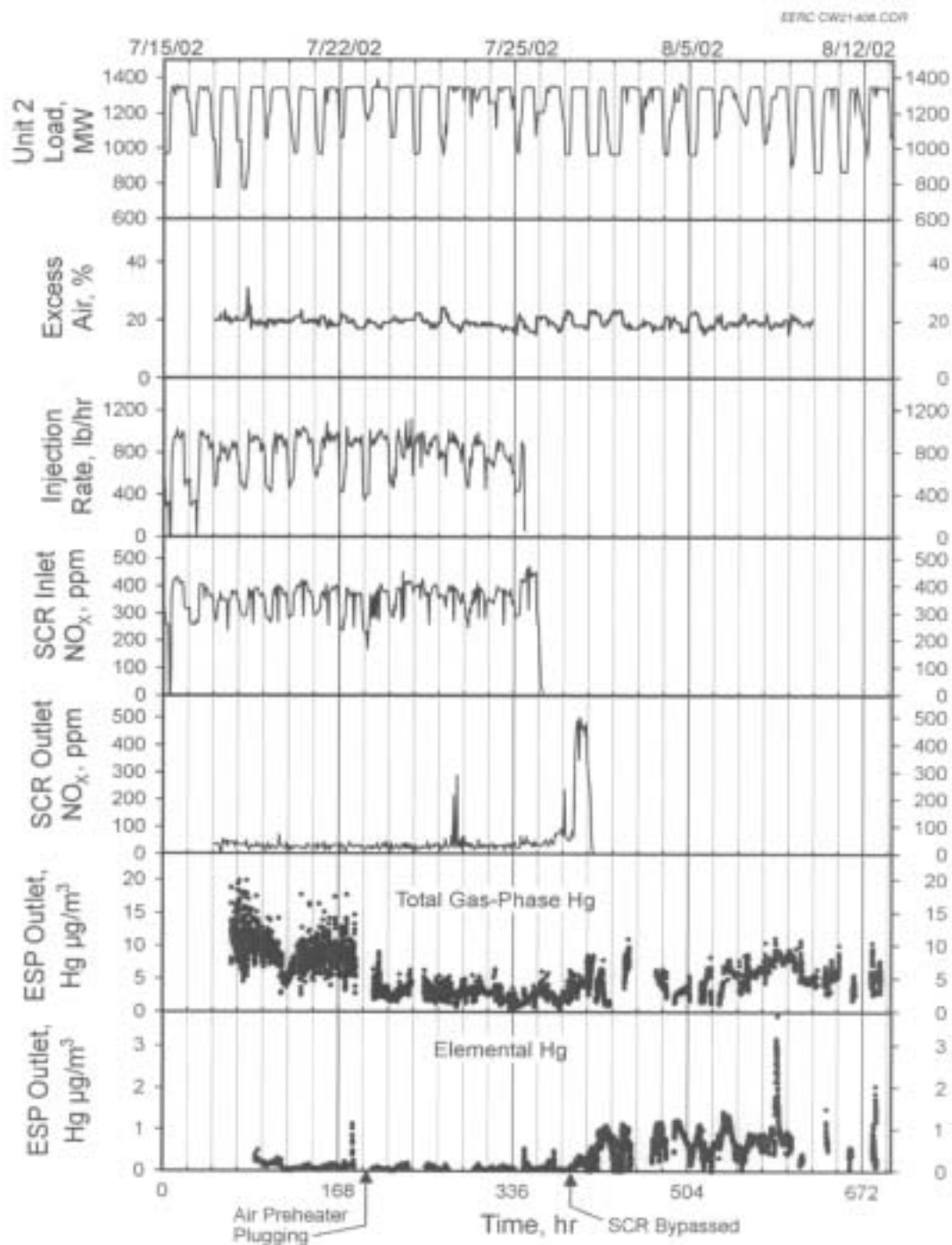


Figure 2-2 (continued)  
Plant Operation Data for Site S2

**Table 2-2**  
**Average Auxiliary Flue Gas Data for Site S2<sup>a</sup>**

Date	Flue Gas Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
SCR Inlet	9.8	2.7803	15.0	3.8
SCR Outlet	10.8	3.3547	14.8	4.6
ESP Inlet	11.3	1.8872	13.9	5.7
ESP Outlet	11.0	0.0021	13.7	5.8
Stack	21.9	0.0016	13.2	6.5

<sup>a</sup> Dust loadings were collected as part of the OH method using EPA Method 17 and, therefore, are not for compliance purposes.

## 2.4 Sampling Results

### 2.4.1 OH Flue Gas Mercury Results

Average Hg results for flue gas sampling at Site S2 are presented in Table 2-3. The complete results are present in Appendix B (Table B-1). As shown in Table 2-3, there was an increase from 54% to 87% in Hg<sup>2+</sup> across the SCR catalyst. This then increased to 97% at the ESP inlet. Total Hg removal was 84%.

**Table 2-3**  
**OH Average and Percentage of Total Mercury Results for S2<sup>a</sup>**

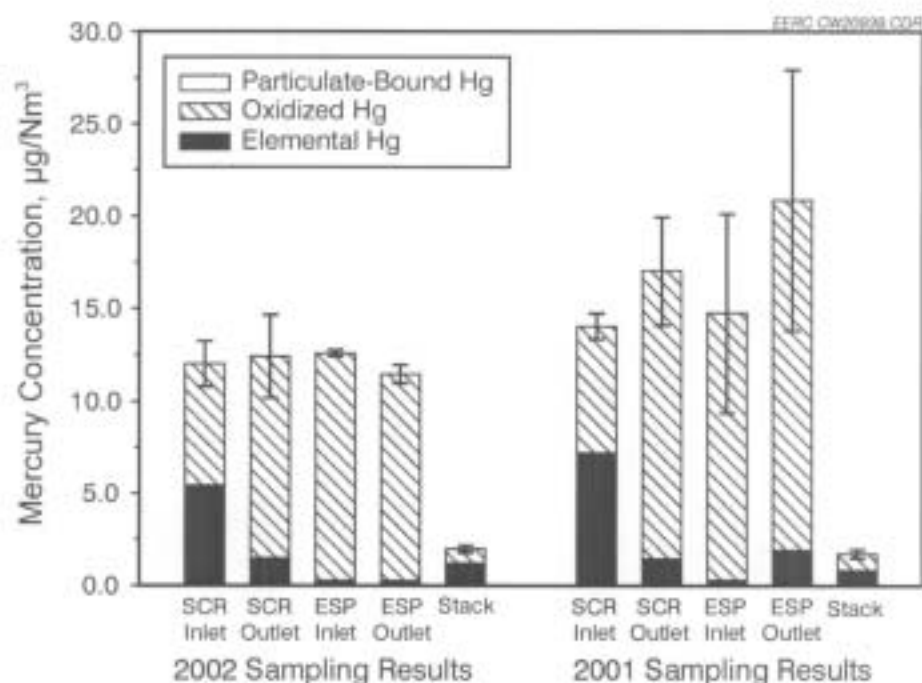
Sample Location	Average, $\mu\text{g}/\text{Nm}^3$				Percent of Total, %		
	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>
SCR Inlet	0.04	6.5	5.5	12.0	0.4	54	46
SCR Outlet	0.06	10.8	1.6	12.4	0.5	87	13
ESP Inlet	0.03	12.2	0.3	12.6	0.2	97	3
ESP Outlet	0.00	11.1	0.3	11.5	0.0	97	3
Stack	0.00	0.7	1.3	2.0	0.2	35	65

Total Mercury Removal = 84%<sup>b</sup>

<sup>a</sup> Hg values are dry and corrected to 3% O<sub>2</sub>.

<sup>b</sup> Total Hg removal is defined as:  $[(\text{ESP Inlet} - \text{Stack})/\text{ESP Inlet}] \times 100\%$ .

A comparison of the 2001 and 2002 results at Site S2 is shown in Figure 2-3. As shown, in 2001 there was an increase from 48% to 91% Hg<sup>2+</sup> across the SCR catalyst, which is a larger change than seen in 2002. It is unknown whether this decrease in Hg oxidation across the SCR catalyst is



**Figure 2-3**  
**Comparison of Mercury Speciation Results 2001 and 2002 for Site S2**

a result of operating the SCR unit over an additional ozone season or due to the modifications that were made for SO<sub>3</sub> mitigation or changes in the coal in 2002.

Although there was a decrease in Hg oxidation across the catalyst, there was no change from 2001 to 2002 in the percentage of Hg<sup>2+</sup> at the ESP inlet location (97% for both years). There was a small decrease in total Hg removal: 89% in 2001 compared to 84% in 2002.

As stated earlier, several operational problems occurred at the plant during the test. Approximately midway through the test period, an increase in pressure drop was measured across the center air heater. To prevent plugging of the air heater, the economizer outlet temperature was raised, and flow through the center air heater was greatly reduced. This eventually required the bypassing of the SCR unit earlier than expected and the load reduced. Therefore, no OH data were obtained in 2002 with SCR bypassed. However, in 2001, the total Hg removal efficiency was only 51% with SCR bypassed.

Although the Hg<sup>2+</sup> concentration at the inlet to the wet FGD (outlet of the ESP) was 97%, only 84% of the Hg was captured by the wet FGD. This appeared to be a result of an increase in Hg<sup>0</sup> at the stack, from 0.3 to 1.3 µg/Nm<sup>3</sup>.

#### 2.4.2 Hg SCEM Results

Two Hg SCEMs were operated at the ESP outlet to gather longer-term variability data. In the original test plan, one Hg SCEM was to be operated at the ESP inlet and one at the ESP outlet. However, because of flue gas chemistry and particulate loading there was severe plugging of the

inertial filter probe so that it was not possible to maintain Hg SCCEM operation at the ESP inlet location. Therefore, the two instruments were operated at the ESP outlet location and configured to operate such that one instrument measured total Hg and the second measured  $\text{Hg}^0$  continuously. With the exception of occasional maintenance routines and troubleshooting, data for both total Hg and  $\text{Hg}^0$  were collected during the entire sampling period. A summary of the Hg SCCEM data is provided in Figure 2-4. As shown in Figure 2-4, there is good agreement between the Hg SCCEM data and the OH data.

It should also be noted that a high amount of variability was observed, especially during the first several days for total Hg concentration. This may be due to continuously switching between measurement of  $\text{Hg}^0$  and total gas-phase Hg during that period as only one Hg SCCEM instrument was monitoring the ESP outlet location for the first 198 hours of the test. The variability of the data reduced noticeably after this period when both instruments were used to monitor each Hg species.

The SCR unit was bypassed midway through the test. Table 2-4 shows the statistical variation of the Hg SCCEM data with and without SCR in service. Based on the Hg SCCEM, there was an increase in  $\text{Hg}^0$  when SCR was bypassed. The concentration of  $\text{Hg}^0$  appears to have increased from  $<0.25 \mu\text{g}/\text{m}^3$  to  $\sim 1 \mu\text{g}/\text{m}^3$  after the SCR unit was bypassed. In Figure 2-5, the percentage of  $\text{Hg}^{2+}$  as determined using the Hg SCCEM ( $\text{total Hg} - \text{Hg}^0$ ) is plotted. When the SCR unit is bypassed, the percentage of  $\text{Hg}^{2+}$  in the flue gas is reduced and appears to become much more variable.



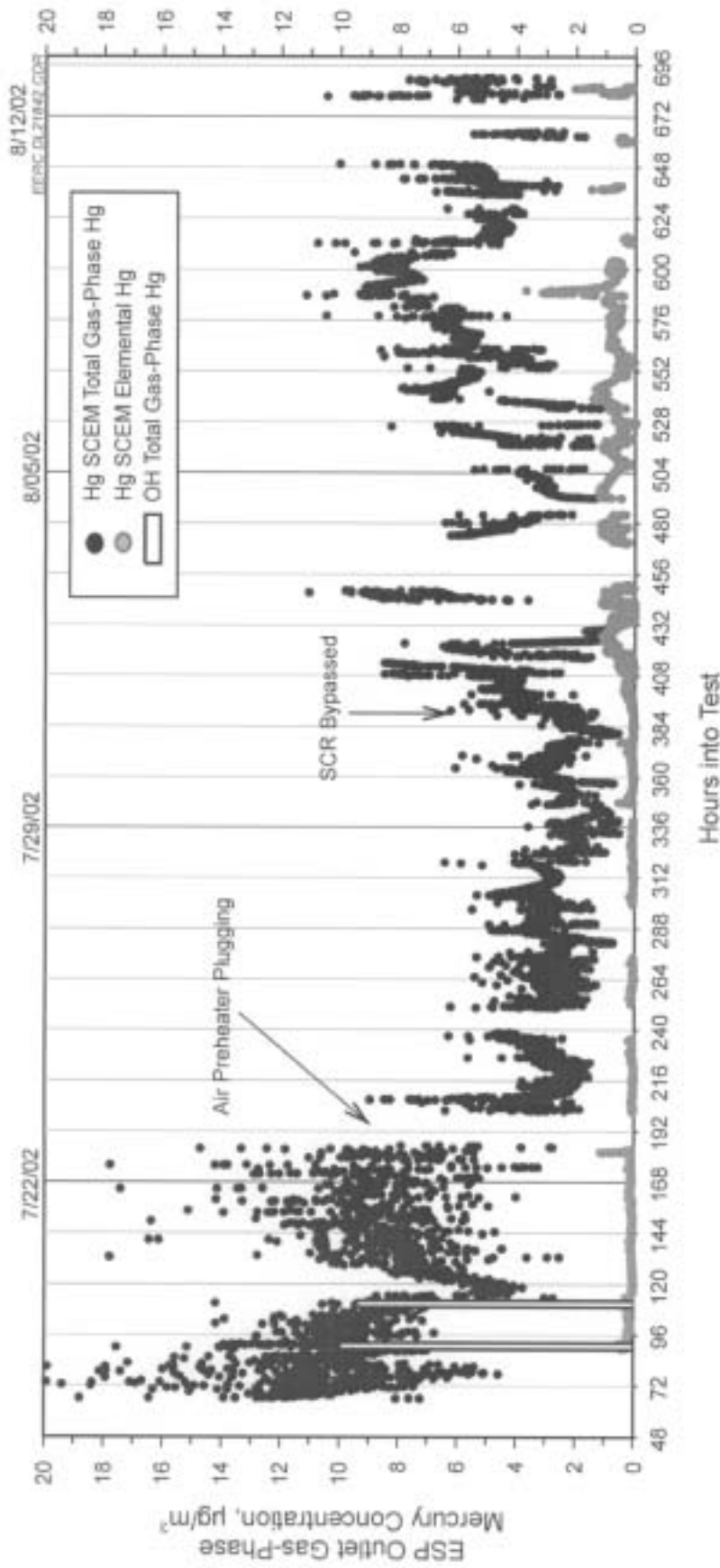
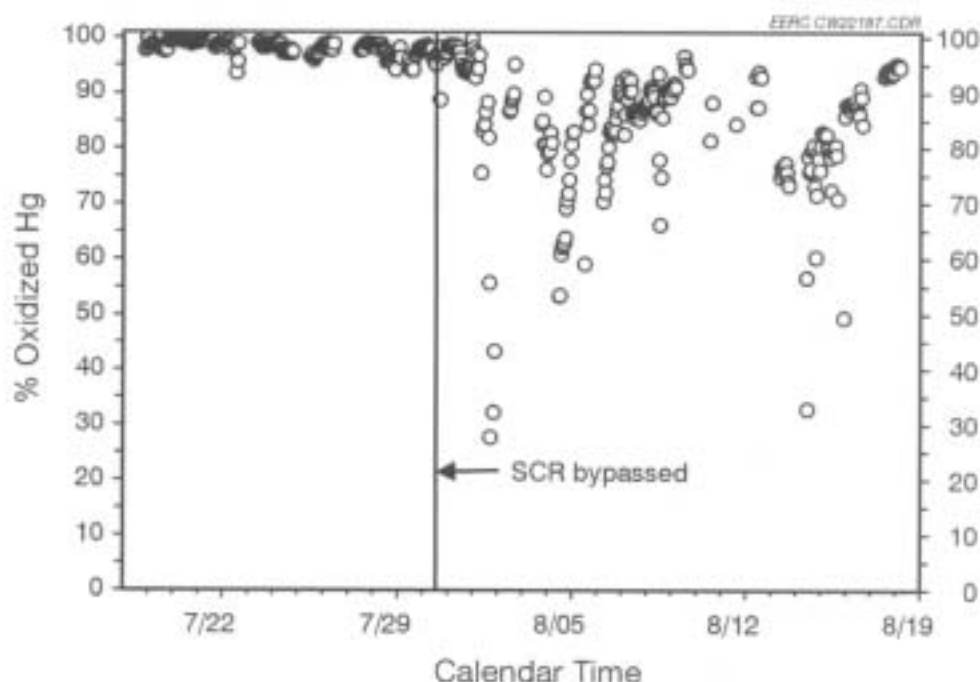


Figure 2-4  
Hg SCEM Results for Site S2

**Table 2-4**  
**Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg**  
**SCEM Data for Site S2**

Mercury	Operation	Average, $\mu\text{g}/\text{m}^3$	Std. Dev., $\mu\text{g}/\text{m}^3$	Upper 90% CI, <sup>a</sup> $\mu\text{g}/\text{m}^3$	Lower 90% CI, $\mu\text{g}/\text{m}^3$
Hg(total)	With SCR	4.7	3.4	10.3	0.0
Hg <sup>0</sup>	With SCR	0.1	0.1	0.3	0.0
Hg(total)	SCR bypassed	6.1	2.0	9.4	2.8
Hg <sup>0</sup>	SCR bypassed	0.8	0.5	1.6	0.0

<sup>a</sup> Confidence interval.



**Figure 2-5**  
**Average Hg<sup>2+</sup> as Measured by Hg SCEMs (total Hg - Hg<sup>0</sup>) for Site S2**

### 2.4.3 Coal Analysis Results

In an attempt to understand the Hg variability observed at Site S2, all of the coal samples (45 coal samples) from Site S2 were analyzed by WE Energies and the EERC for Hg and chloride content. The complete data set is presented in Appendix B, Table B-2. The average Hg concentration and chloride content of the coal were relatively constant during the 4-week test period. The Hg concentration was  $0.12 \pm 0.02 \mu\text{g}/\text{g}$ , and the chloride content was  $636 \pm 44 \text{ ppm}$ . Both values are similar to those collected during the previous year's sampling. Table 2-5 presents the proximate and ultimate analyses for the period during which the OH sampling was done.

**Table 2-5**  
**Coal Analysis for Site S2<sup>a</sup>**

Date		7/17/02	7/18/02	7/19/02	7/20/02	Avg.
Mercury	ppm (dry)	0.13	0.11	0.11	0.13	0.12
Chlorine	ppm (dry)	724	605	593	609	632
<i>Proximate Analysis</i>						
Moisture	wt%	5.6	5.4	6.7	6.8	6.1
Volatile Matter	wt%	39.0	39.7	39.8	40.2	39.7
Fixed Carbon	wt%	46.5	45.0	44.1	43.8	44.8
Ash	wt%	8.9	9.9	9.5	9.2	9.4
<i>Ultimate Analysis</i>						
Hydrogen	wt%	5.4	5.4	5.4	5.4	5.4
Carbon	wt%	69.6	68.3	66.5	66.8	67.8
Nitrogen	wt%	1.5	1.4	1.3	1.3	1.4
Sulfur	wt%	3.6	4.0	4.0	3.8	3.9
Oxygen	wt%	11.0	11.0	13.3	13.5	12.2
Heating Value	Btu/lb	12,438	12,070	11,938	11,940	12,097
F <sub>d</sub> Factor <sup>b</sup>	dscf/10 <sup>6</sup> Btu	9915	10,069	9860	9876	9930

<sup>a</sup> Except where stated, all results are on an as-received basis.

<sup>b</sup> As defined in EPA Method 19.

#### 2.4.4 ESP Ash and FGD Mercury Results

ESP hopper ash samples were collected daily as a field composite of ash from hoppers associated with the first field of both the upper and lower ESP. These samples were analyzed for Hg and loss on ignition (LOI). The FGD samples were filtered, and the liquid and solid fractions both analyzed for Hg. A summary of the analysis of the ESP hopper ash and FGD samples is provided in Table 2-6.

The average Hg concentration in the ESP hopper ash was low, 0.05 µg/g. This is consistent with the particulate-bound Hg measured in the flue gas at the ESP inlet. The LOI was also very low, 0.8%. One factor which may impact the ability of a fly ash to adsorb Hg is the carbon content of the ash. Although not directly measured, the very low LOI indicates low carbon content in the ash. Both the Hg and LOI results are consistent with the data obtained in 2001. For the FGD samples, the average Hg concentration was 0.15 µg/g.

**Table 2-6**  
**Analysis of ESP Hopper Ash and FGD Material for Site S2**

Date	ESP Hopper Ash		Hg in FGD Material, $\mu\text{g/g}$ Solids, %	
	Hg, $\mu\text{g/g}$	LOI, %		
7/16/02	0.025	0.97		
7/17/02	0.034	0.51	0.16	17.3
7/18/02	0.072	1.15	0.14	18.5
7/19/02	0.032	0.68	0.16	16.5
7/22/02	0.049	0.71		
7/23/02	0.140	1.16	0.12	16.0
Average	0.059	0.86	0.15	17.1

#### 2.4.5 $\text{NH}_3$ Slip and $\text{SO}_3$ Flue Gas Results

$\text{NH}_3$  slip testing was conducted at the SCR and ESP outlets and the  $\text{SO}_3$  testing at the SCR outlet location. A summary of these results is provided in Table 2-7. The  $\text{NH}_3$  slip concentrations were low, less than 1 ppm. In general, low  $\text{NH}_3$  slip values are representative of an efficiently performing SCR.

**Table 2-7**  
 **$\text{NH}_3$  Slip and  $\text{SO}_3$  Results at Site S2<sup>a</sup>**

Date	$\text{NH}_3$ Slip, ppm		$\text{SO}_3$ , ppm
	SCR Outlet	ESP Outlet	SCR Outlet
07/16/02	0.48		
07/17/02	0.47		30.2
07/18/02			983 <sup>b</sup>
07/19/02			1141 <sup>b</sup>
07/20/02		0.52	
07/20/02		0.56	

<sup>a</sup> Dry and 3%  $\text{O}_2$ .

<sup>b</sup> These two values appear to be outliers.

Unfortunately, there appears to be some contamination in two of the  $\text{SO}_3$  values. It is unlikely that the  $\text{SO}_3$  concentration in the flue gas is greater than 900 ppm. A careful review of the procedures, sample sheets, and analysis did not provide an obvious explanation. One data point

(30.2 ppm) from the SCR outlet was similar to data collected from 2001 and is consistent with expected values. The average ESP outlet  $\text{SO}_3$  value in 2001 was 33.2 ppm.

## 2.5 Mercury Mass Balance

The average ESP hopper ash results were compared with flue gas Hg measurements from the ESP inlet and outlet to determine the Hg mass balance across the ESP. The sum of the ESP hopper ash (in  $\mu\text{g}/\text{Nm}^3$  of flue gas as calculated from the dust loading) and the ESP outlet Hg concentration divided by the ESP inlet Hg concentration results in a balance of 94% (from Table 2-3).

To compare the available Hg in the coal to flue gas measurements, emission factors ( $F_d$  factors) as calculated using EPA Method 19 were used to estimate the coal-based Hg concentration. Using the average coal Hg concentration and  $F_d$  factors results in a flue gas concentration of  $10.9 \text{ lb}/10^{12} \text{ Btu}$ . This compares to a flue gas Hg measurement at the ESP inlet of  $9.1 \text{ lb}/10^{12} \text{ Btu}$ , giving a balance of 83%.

The plant did not provide information as to the rate at which FGD material was produced. Therefore, it is not possible to do a mass balance around the wet FGD. However, using the  $F_d$  factors, the flue gas Hg measurements at the stack averaged  $1.43 \text{ lb}/10^{12} \text{ Btu}$  which corresponds to a removal of 87% (based on the coal Hg) compared to a measured Hg removal of 84%.

## 2.6 General Observations from S2

- There was increased Hg oxidation across the SCR catalyst as the percentage of  $\text{Hg}^{2+}$  in the flue gas increased from 54% to 87%. At the ESP inlet and outlet location, the percentage of  $\text{Hg}^{2+}$  was 97%.
- Comparing the 2002 results with those obtained in 2001 indicated a small decrease in the Hg oxidation across the SCR catalyst. In 2001, there was an increase from 48% to 91% in  $\text{Hg}^{2+}$  compared to an increase from 54% to 87% in 2002. It is unknown if this is due to a catalyst-aging effect, changes in the operation of the SCR unit (lower temperature), or the addition of alkali upstream of the SCR unit. Although there was a slight decrease in Hg oxidation across the catalyst, the percentage of  $\text{Hg}^{2+}$  at the ESP inlet location was the same in 2002 and 2001: 97%. The overall Hg removal at Site S2 averaged 84% in 2002 compared to 87% in 2001.
- There appeared to be some reemission of Hg across the wet FGD. The  $\text{Hg}^0$  increased from  $0.3 \mu\text{g}/\text{Nm}^3$  at the inlet to the wet FGD to  $1.3 \mu\text{g}/\text{Nm}^3$  at the stack. However, this is within the variability of the data.
- Operational changes during the month resulted in data variability; however, those fluctuations resulted from acknowledged changes in system operation and do not represent steady state.
- OH results correlated well with Hg SCCEM data and were consistent with repeated samples.
- Very little, if any, Hg was removed across the ESP.

# 3

## SITE S4

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Site S4 was selected to provide data to determine the impact of catalyst aging on the potential of the SCR units to oxidize Hg. The mercury sampling and analysis at this site was conducted by Western Kentucky University and was sponsored by EPRI and the host utility.

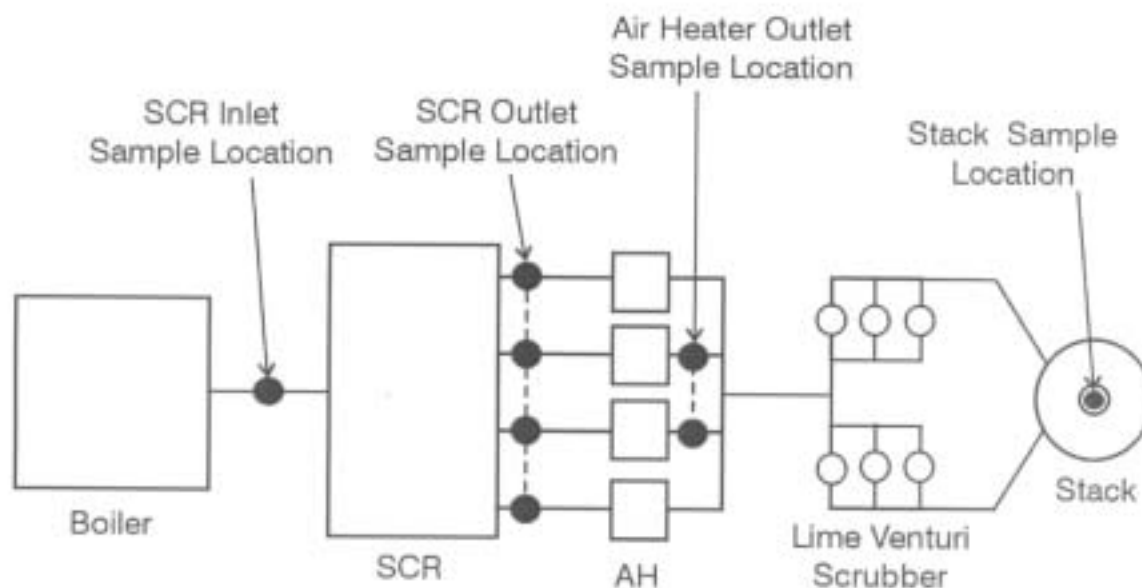
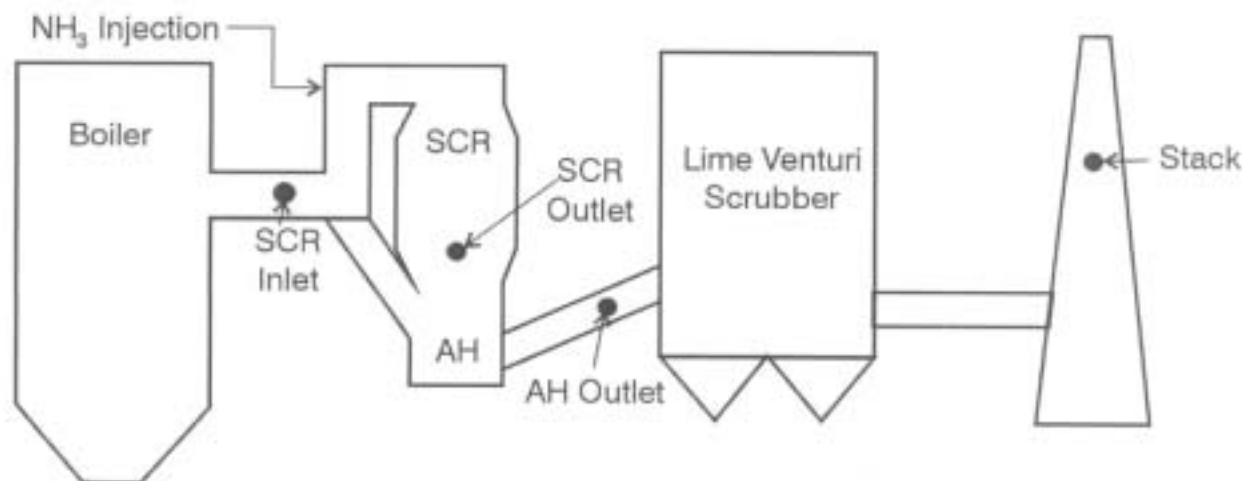
### 3.1 Site Description and Configuration

Site S4 is a cyclone boiler that fires a Kentucky bituminous coal and employs SCR followed by a combined particulate/SO<sub>2</sub> venturi/spray tower scrubber (for purposes of this report, this will be referred to as a venturi scrubber). The venturi scrubber has a total of six modules. The system achieves a high particulate removal using a venturi to generate very small water droplets that create a high relative velocity between the particle and droplets. Some of the scrubbing slurry containing limestone for SO<sub>2</sub> removal is introduced at the top of the converging venturi section. However, most of the limestone slurry is introduced through conventional spray nozzles attached to three spray headers in the annular spray tower section of the scrubber. The scrubbed gas and entrained droplets enter a separator before the flue gas exits the stack. The spent slurry is discharged to an on-site disposal pond.

The SCR unit at S4 has a space velocity of 2275 hr<sup>-1</sup> and contains a vanadium/titanium honeycomb catalyst manufactured by Cormetech. The catalyst is spread into three layers in the SCR unit. The NH<sub>3</sub>-to-NO<sub>x</sub> ratio was specified to be 1.0. The unit is designed to be operated only during the ozone season (May 1–September 30) (To use all the NH<sub>3</sub> on-site, the SCR was operated 15 additional days in 2002 in October). During the remainder of the year, the SCR is bypassed, but continually pressurized with heated ambient air. Prior to testing in 2002, the SCR unit had been operated for approximately two ozone seasons. Flue gas testing was conducted with SCR operating normally and again with SCR bypassed. General information about the unit configuration is below:

- Fuel type: Kentucky bituminous coal
- Boiler capacity: 704 MW gross
- Boiler type: cyclone boiler with overfire air to reduce NO<sub>x</sub>
- NO<sub>x</sub> control: SCR
- SO<sub>2</sub> and particulate control: combined particulate/SO<sub>2</sub> venturi/spray tower scrubber

A schematic of Site S4, including sample locations, is shown in Figure 3-1.



**Figure 3-1**  
**Schematic of Site S4 Showing Sample Locations from a Vertical and Horizontal Perspective**

### 3.2 Sampling Approach

Sampling at S4 was conducted similar to testing conducted the previous year and documented in *Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury* [11]. The objective of testing this unit again in 2002 was to evaluate the effect of catalyst aging on speciated Hg emissions.

### 3.2.1 Flue Gas Sample Streams

With SCR in service, flue gas Hg speciation was measured at four locations using the OH method, the SCR inlet and outlet, the outlet of the air preheater (venturi scrubber inlet), and the stack. With SCR out of service, sampling was only done at the air preheater outlet and stack. These locations are identified in Figure 3-1. A test matrix is provided in Table 3-1. To best quantify the effect SCR and the venturi scrubber had on Hg speciation and concentration, OH measurements were completed as paired sets across each device. In addition to Hg measurements, flue gas sampling was done to measure particulate loading, SO<sub>3</sub> concentration, and NH<sub>3</sub> slip.

**Table 3-1**  
**Sampling Test Matrix for Site S4**

Date		SCR In	SCR Out	ESP In	Stack	SCR In	SCR Out	SCR Out
Begin	End	OH	OH	OH	OH	SO <sub>3</sub>	SO <sub>3</sub>	NH <sub>3</sub>
<i>With SCR</i>								
09/11/02	09/13/02	3	3	3	3	2	2	2
<i>Without SCR</i>								
10/16/02	10/17/02			3	3			

Longer-term Hg monitoring was conducted using an Hg SCCEM (PSA) located at the air heater outlet (same as the venturi scrubber inlet) location. Except for periods of maintenance and when the unit was down, the Hg SCCEM was operated around the clock for the duration of the project.

### 3.2.2 Other Sample Streams

To determine the fate of Hg throughout the unit, samples of coal and venturi scrubber slurry were taken and analyzed for total Hg. A coal sample, taken from the coal yard, was associated with each day of OH sampling. The venturi scrubber samples were taken as the slurry was drained to the settling tank.

## 3.3 Process Operating Conditions

Plant operational data are presented in Figure 3-2 for Site S4. It should be noted, with the exception of load and boiler O<sub>2</sub> data, the operational data were only collected by the plant during the period when the OH sampling was conducted (beginning and end of test). As the figure shows, the operation at Site S4 during this test program was representative of normal daily operation at or near full load, and there was little variation in the 45 days of the test program, excluding when the unit was down for 3 days. The NO<sub>x</sub> removal efficiency for the SCR unit averaged 87%.



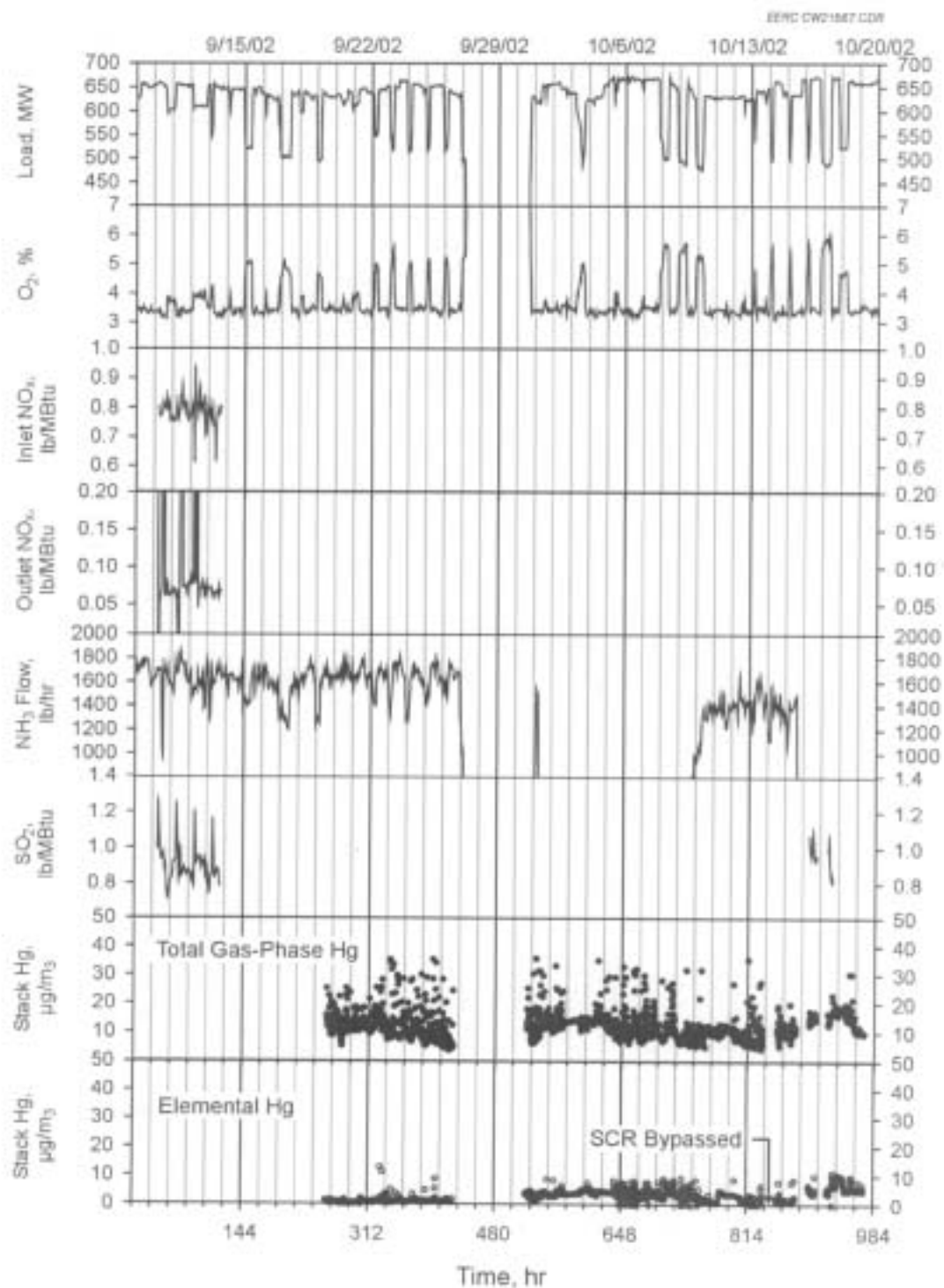


Figure 3-2

Plant Operation Data for Site S4 (note the plant logged some of the data, i.e., SCR inlet and outlet NO<sub>x</sub>, only when the OH samples were being done)

The average auxiliary flue gas data for Site S4 are shown in Table 3-2. The complete data set is shown in Appendix C, Table C-2. The excess  $O_2$  at the boiler exit was  $3.7\% \pm 0.8\%$  over the entire sampling period of 45 days. However, as is typical at most power plants, there is a substantial air leak across the air preheater. Based on the measured  $O_2$  at the air heater outlet/venturi scrubber inlet, the average excess  $O_2$  was 7.2%. The air leakage across the SCR and venturi scrubber was minimal. The particulate removal efficiency of the venturi scrubber is high, >99.9%.

**Table 3-2**  
**Average Auxiliary Flue Gas Data for Site S4<sup>a</sup>**

Date	Flue Gas Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>With SCR in Service</i>				
SCR Inlet	10.2	1.93	15.0	3.9
SCR Outlet	9.5	1.39	14.9	3.9
Air Preheater Outlet	8.7	1.10	9.0	10.7
Stack	15.2	0.00 <sup>b</sup>	11.4	7.8
<i>With SCR Bypassed</i>				
Air Preheater Outlet	9.1	1.24	11.1	7.9
Stack	14.0	0.01 <sup>b</sup>	11.1	7.9

<sup>a</sup> Dust loadings were collected as part of the OH method using EPA Method 17 and, therefore, are not for compliance purposes.

<sup>b</sup> Measured to only two significant digits (1/100 of a gram).

## 3.4 Sampling Results

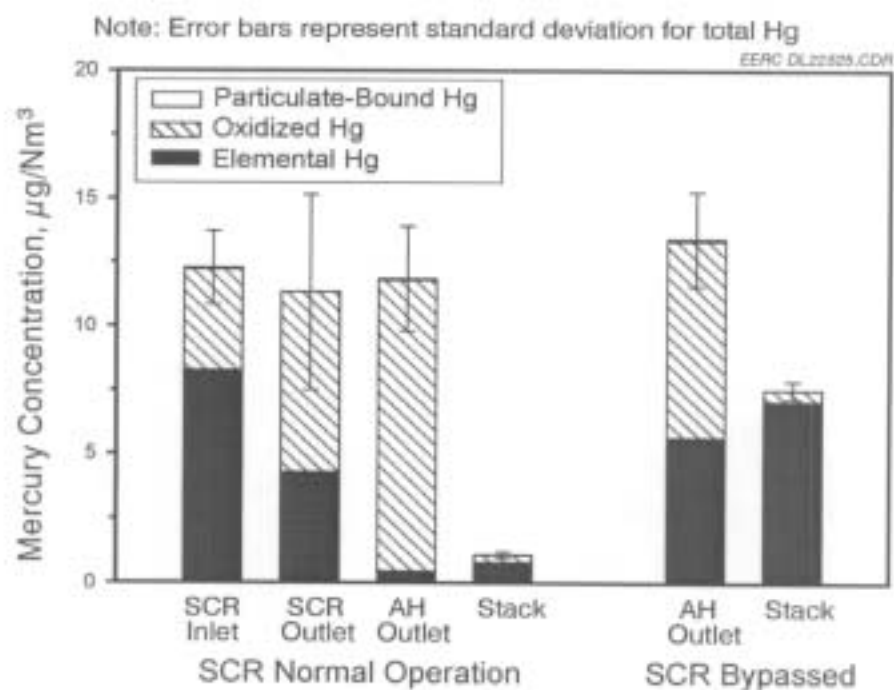
### 3.4.1 OH Flue Gas Mercury Results

The Hg results for Site S4 with the averages and percentage of each species are shown in Table 3-3. The complete OH results for Site S4 are shown in Appendix B, Tables B-3 and B-4. Figure 3-3 shows a comparison of the data with SCR in service and with the SCR unit bypassed. As shown in Table 3-3, significant oxidation occurs across the SCR catalyst, from 33%  $Hg^{2+}$  to 63%  $Hg^{2+}$ . The percentage of  $Hg^{2+}$  is further increased to 96% at the outlet of the air preheater. The overall Hg removal is 91% when SCR is in service compared to only 44% when the SCR unit is bypassed.

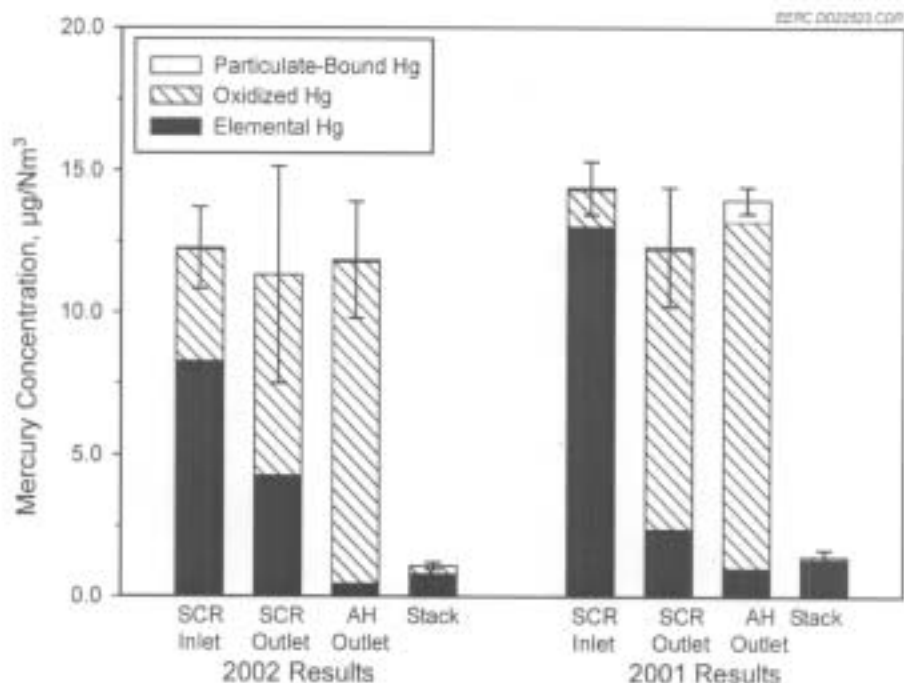
A comparison of the 2001 and 2002 results at Site S4 is shown in Figure 3-4. As can be seen in the figure, there was a decrease in the oxidation across the SCR catalyst in 2002. In 2001, the concentration of  $Hg^{2+}$  as a percentage of total Hg increased from 9% to 80% across the SCR catalyst. This is compared to only 33% to 63% in 2002. However, there is no significant difference between 2001 and 2002 results as measured at the air preheater outlet location; also,

**Table 3-3**  
**Average OH Mercury and Results for Site S4**

Sample Location	Average OH Hg Results				Percent of Total Hg, %		
	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg(total)	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>
<i>With SCR in Service</i>							
SCR Inlet	0.05	4.0	8.3	12.3	0	33	67
SCR Outlet	0.00	7.1	4.3	11.4	0	63	37
AH Outlet	0.06	11.3	0.5	11.8	0	96	4
Stack	—	0.3	0.8	1.1	—	27	73
Total Mercury Removal = 91%							
<i>With SCR Bypassed</i>							
AH Outlet	0.08	7.7	5.6	13.4	1	57	42
Stack	NV	0.5	7.1	7.5	—	7	93
Total Mercury Removal = 44%							



**Figure 3-3**  
**Comparison of Mercury Speciation Results with the SCR in Service and with the SCR Bypassed**



**Figure 3-4**  
**Comparison of Mercury Speciation Results 2001 and 2002 for Site S4**

the overall Hg removal was the same in 2002 as compared to 2001: 91% compared to 90%. There is some question whether the decrease in Hg oxidation across the catalyst is due to catalyst aging or some other factor. As will be discussed later in this section, the chloride content of the coal appeared to vary considerably in 2001 and was more consistent in 2002. This variation may have affected the Hg oxidation across the SCR catalyst.

As discussed in Section 2.4.1 (Site S2), it appears that Hg reemission can occur across a wet FGD system. At Site S4, there is an increase in the concentration of  $\text{Hg}^0$  across the venturi scrubber; however, it is very small (0.5 to 0.8  $\mu\text{g}/\text{Nm}^3$ ) and is within the variation of the data. This is discussed in more detail in Section 6.4.

### 3.4.2 Hg SCCEM Results

A Hg SCCEM was operated at the air heater outlet location at Site S4. In an effort to gather longer-term data, the Hg CEM was operated nearly continuously for the duration of the project, except when the boiler was down (the Hg SCCEM was operated to alternate between total Hg and  $\text{Hg}^0$ ). A summary of Hg SCCEM data plotted over the entire test period is provided in Figure 3-5. There is significant variability in both the total Hg and  $\text{Hg}^0$  data. Table 3-4 shows the statistical variation of the SCCEM data with and without SCR in service. Based on the Hg SCCEM data, there was an increase in the average  $\text{Hg}^0$  when the SCR unit was bypassed at about 880 hours into the test, from 2.26 to 6.3  $\mu\text{g}/\text{m}^3$ . In Figure 3-6, the percentage of  $\text{Hg}^{2+}$  as determined using the Hg SCCEM (total Hg -  $\text{Hg}^0$ ) is plotted. Figure 3-2 clearly shows substantial  $\text{Hg}^{2+}$  variability.

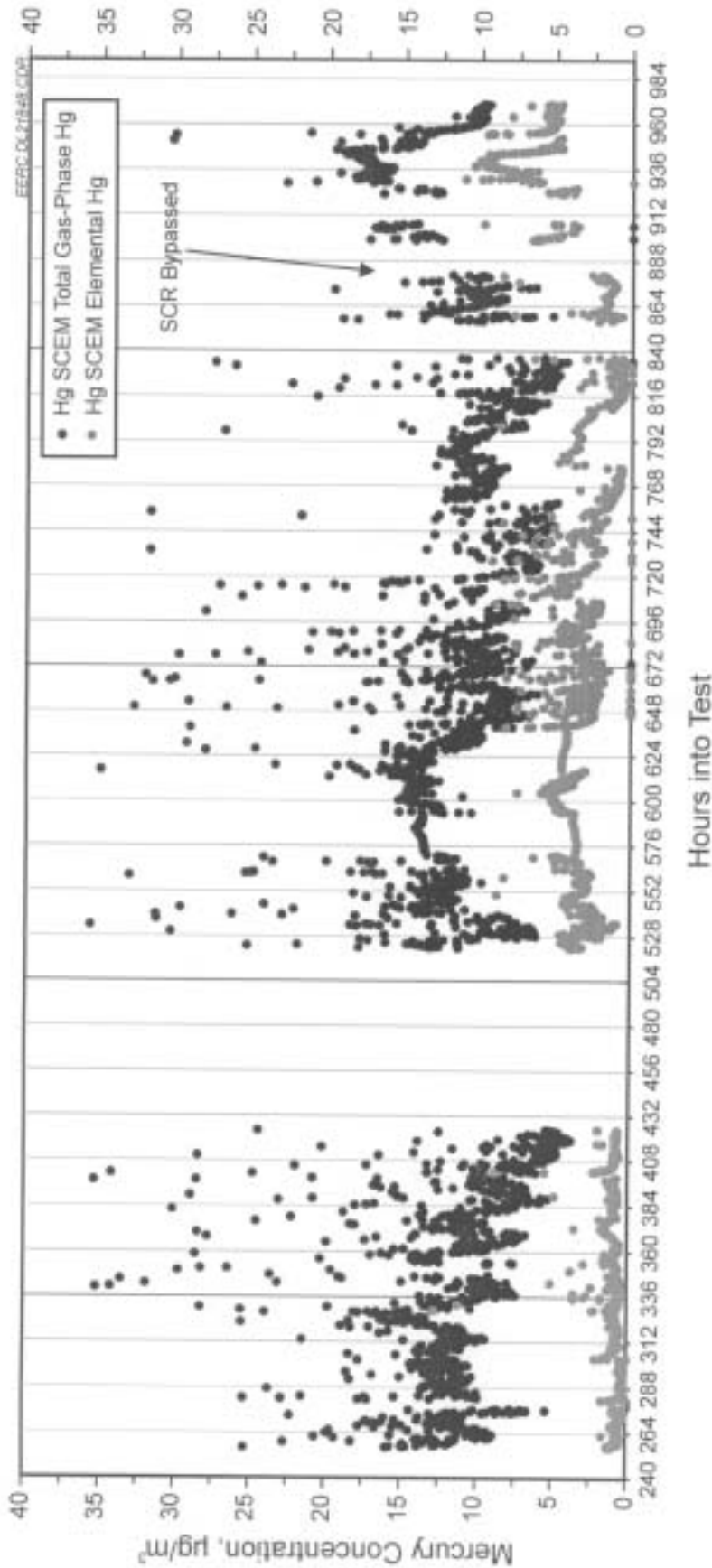
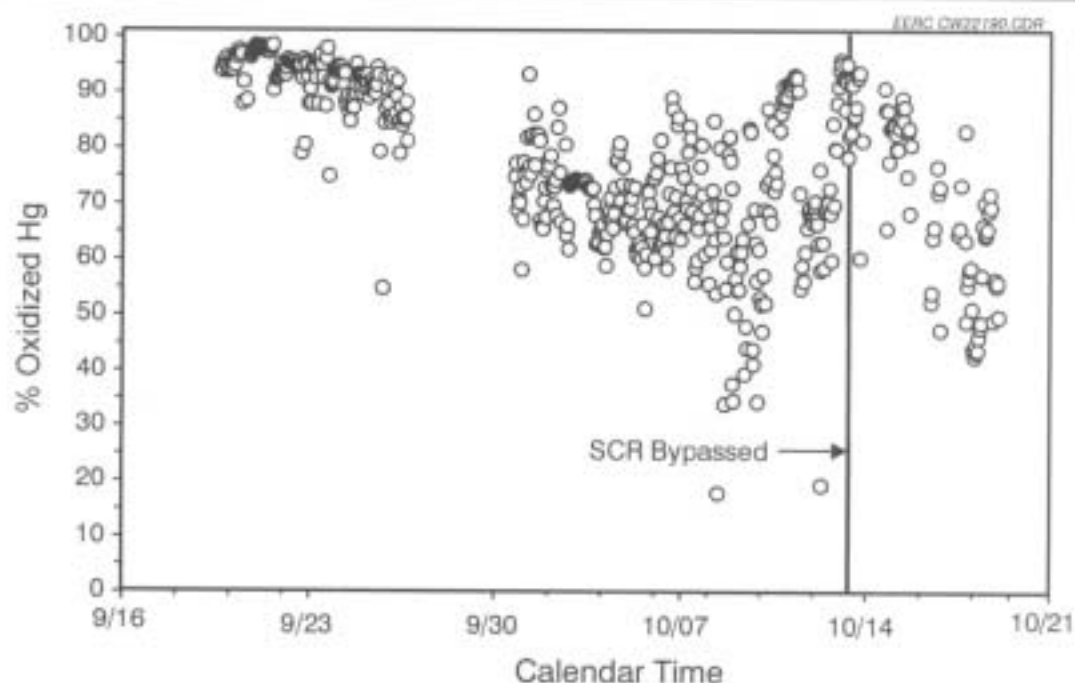


Figure 3-5  
Hg SCEM Results for Site S4

**Table 3-4**  
**Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg**  
**SCEM Data for Site S4**

Mercury	Operation	Average, $\mu\text{g}/\text{m}^3$	Std. Dev., $\mu\text{g}/\text{m}^3$	Upper 90% CI, $\mu\text{g}/\text{m}^3$	Lower 90% CI, $\mu\text{g}/\text{m}^3$
Hg(total)	With SCR	11.5	4.5	18.5	4.1
Hg <sup>0</sup>	With SCR	2.3	1.7	5.1	0.0
Hg(total)	SCR bypassed	14.6	3.6	20.5	8.7
Hg <sup>0</sup>	SCR bypassed	6.3	1.9	9.4	3.2



**Figure 3-6**  
**Average Hg<sup>2+</sup> as Measured by Hg SCEMs (Total Hg-Hg<sup>0</sup>) for Site S4**

### 3.4.3 Coal Analysis Results

As stated in Section 3.1, Site S4 burns a medium-sulfur Kentucky bituminous coal in a cyclone boiler. The analysis of the coal fired is shown in Table 3-5. The coal analysis shows that the coal was relatively constant in 2002. However, in 2001 at Site S4, the chloride content in the coal increased from an average of 360 ppm with SCR in service to 1160 with SCR bypassed. Therefore, it is possible that some of the differences in Hg oxidation across the SCR catalyst between the 2001 and 2002 testing may be due to differences in the coal.

**Table 3-5**  
**Coal Analysis for Site S4<sup>a</sup>**

Date	9/11/2002	9/12/2002	9/13/2002	10/16/2002	10/17/2002
Mercury ppm (dry)	0.17	0.16	0.15	0.19	0.14
Chlorine ppm (dry)	269	228	241	270	295
<b>Proximate Analysis</b>					
Moisture, wt%	12.3	12.6	11.8	11.3	11.2
Volatile Matter, wt%	35.1	35.3	35.5	35.5	35.5
Fixed Carbon, wt%	44.1	43.4	43.8	45.0	45.0
Ash, wt%	8.5	8.7	8.8	8.2	8.4
<b>Ultimate Analysis</b>					
Hydrogen, wt%	6.8	6.9	6.8	5.6	5.5
Carbon, wt%	65.7	66.3	66.5	74.6	77.2
Nitrogen, wt%	1.3	1.3	1.3	1.6	1.9
Sulfur, wt%	2.8	2.7	2.8	2.8	2.7
Oxygen, wt%	14.1	13.8	13.1	7.0	4.9
Heating Value, Btu/lb	11,597	11,468	11,409	11,852	11,848
F <sub>as</sub> <sup>b</sup> dscf/10 <sup>6</sup> Btu	10,397	10,664	10,733	11,217	11,592

<sup>a</sup> Except where stated, all results are on an as-received basis.

<sup>b</sup> As defined in EPA Method 19.

#### **3.4.4 Mercury Collected by the Venturi Scrubber**

As shown in Table 3-6, there appears to be less Hg captured by the venturi scrubber when the SCR is bypassed, as expected.

**Table 3-6**  
**Partitioning of Mercury in Material Collected from Venturi Scrubber**

Date	Hg in FGD Material, $\mu\text{g/g}$	Solids, %
9/11/2002	0.14	15.6
9/12/2002	0.11	16.2
9/12/2002	0.10	14.3
9/13/2002	0.08	15.2
10/16/2002	0.03	12.4
10/17/2002	0.04	12.5

### 3.4.5 $\text{NH}_3$ Slip and $\text{SO}_3$ Flue Gas Results for Site S4

The results for  $\text{NH}_3$  slip and  $\text{SO}_3$  concentrations for each of the tests conditions are shown in Table 3-7. The  $\text{NH}_3$  slip concentrations are low (<2 ppm), indicating a well-performing SCR. This is also shown by 87%  $\text{NO}_x$  removal efficiency. Within the statistical variation of the measured values, the  $\text{SO}_3$  concentration at the SCR outlet and inlet locations were the same. At Site S4, it does not appear SCR increased the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . Results were similar to those obtained from testing conducted in 2001.

**Table 3-7**  
**S4 Flue Gas,  $\text{NH}_3$  Slip, and  $\text{SO}_3$  Results for Site S4\***

Test Condition	Date	$\text{NH}_3$ Slip SCR Outlet, ppm	$\text{SO}_3$ SCR Inlet, ppm	$\text{SO}_3$ SCR Outlet, ppm
SCR On-Line	9/11/2002	0.04	10.9	14.4
SCR On-Line	9/11/2002	0.18	13.4	10.3
SCR On-Line	9/11/2002	1.33	—	—

\* All results are reported on a dry, 3%  $\text{O}_2$  basis.

## 3.5 Mercury Mass Balance

The Hg balance is determined by comparing the concentration of Hg in sources entering the plant to the concentration of Hg in the sources emitted from the plant. Site S4 has a venturi scrubber. Without information regarding scrubber flow, slurry, and blowdown rates, it is not possible to do a mass balance around the FGD. The average  $F_d$  factors for Site S4 are shown in Table 3-8. A Hg balance comparing the measured Hg in the flue gas at the air heater outlet location compared to the Hg generated by the coal is 86% with SCR and 99% for the test conducted with SCR bypassed.



**Table 3-8**  
**Average Mercury Emission Factors for Site S4**

	Coal, lb/10 <sup>12</sup> Btu	Air Preheater Outlet, lb/10 <sup>12</sup> Btu	Stack, lb/10 <sup>12</sup> Btu	Overall Hg Removal, %
With SCR in Service	10.8	9.3	0.9	92
With SCR Bypassed	10.8	10.5	6.9	45

### 3.6 General Observations from S4

- There was increased Hg oxidation across the SCR catalyst as the percentage of Hg<sup>2+</sup> in the flue gas increased from 32% at the SCR inlet to 62% at the outlet. At the air preheater outlet location, the percentage was 96%.
- Comparing the 2002 results with those obtained in 2001 indicated that the percentage of Hg oxidation that occurred across the SCR unit in 2001 decreased. It is unknown if this is due to a catalyst-aging effect or changes in the coal composition, in particular the chloride concentration. Although there was a decrease in Hg oxidation across the catalyst, the overall Hg removal at Site S4 did not change: 91% in 2002 compared to 90% in 2001.
- Comparing the Hg speciation results (at the air preheater outlet location) with and without the SCR in service showed that the presence of the SCR unit resulted in increased Hg oxidation from 57% without SCR to 96% with SCR. As a result, the overall Hg removal across the venturi scrubber increased from 44% to 91%, when the SCR was in service.
- Although there was an increase in Hg<sup>0</sup> across the venturi scrubber, it was very small: 0.5 to 0.8 µg/Nm<sup>3</sup>. This is within the variability of the data.
- There was substantial variability in Hg and Hg speciation as measured using the Hg SCEMs.
- Based on the measurement, it appears that the SCR unit did not result in SO<sub>2</sub> to SO<sub>3</sub> oxidation (note: these results are similar to those generated in 2001).

# 4

## SITE S5

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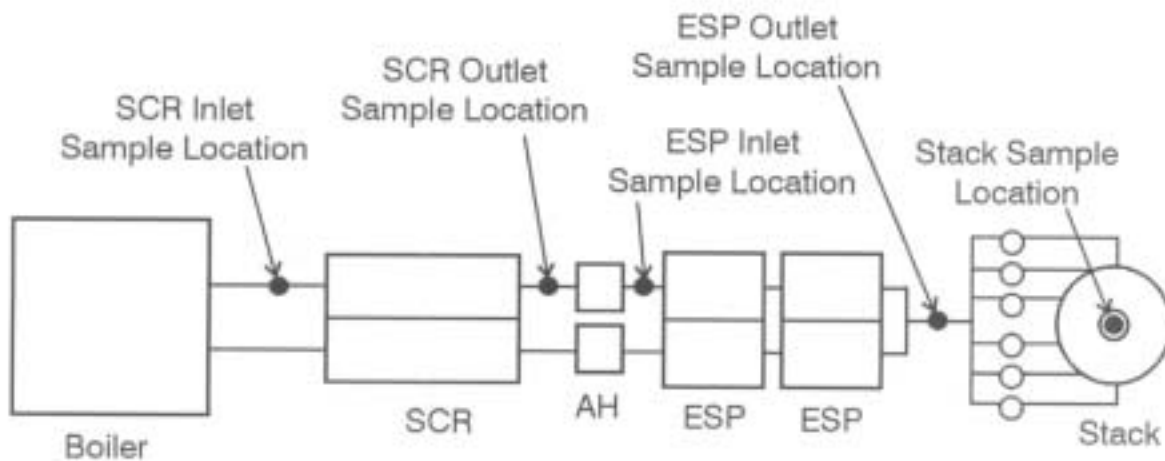
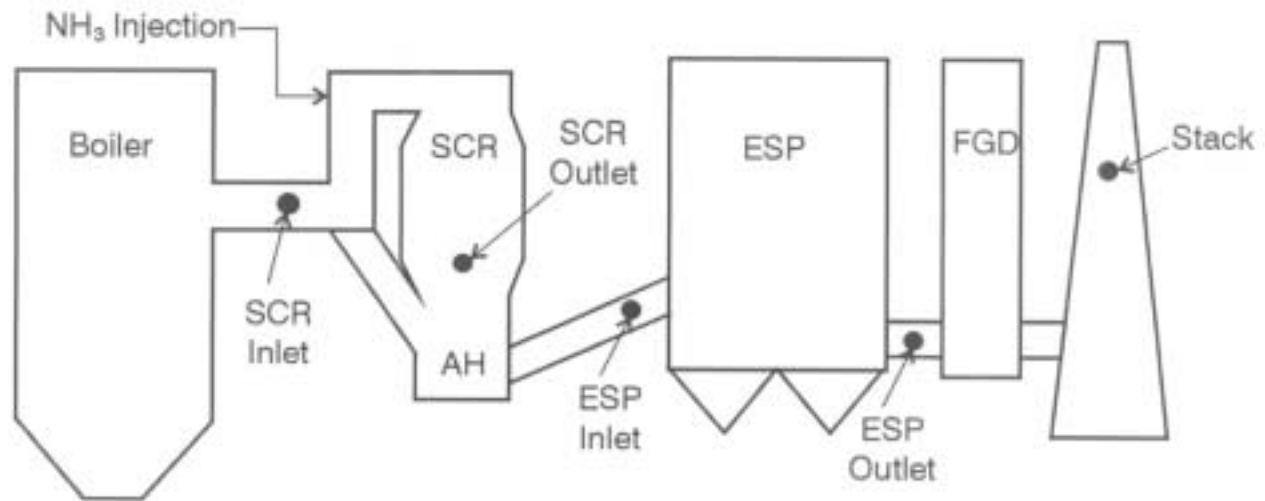
Site S5 was selected for inclusion in the 2002 SCR testing program to provide additional data on the effect of SCR on speciated Hg emissions for an eastern bituminous coal with a wet FGD, in particular how it impacts the Hg removal across a wet FGD. Two “sister” units were tested at Site S5. They are essentially the same design except one does not have an SCR unit.

### 4.1 Site Description and Configuration

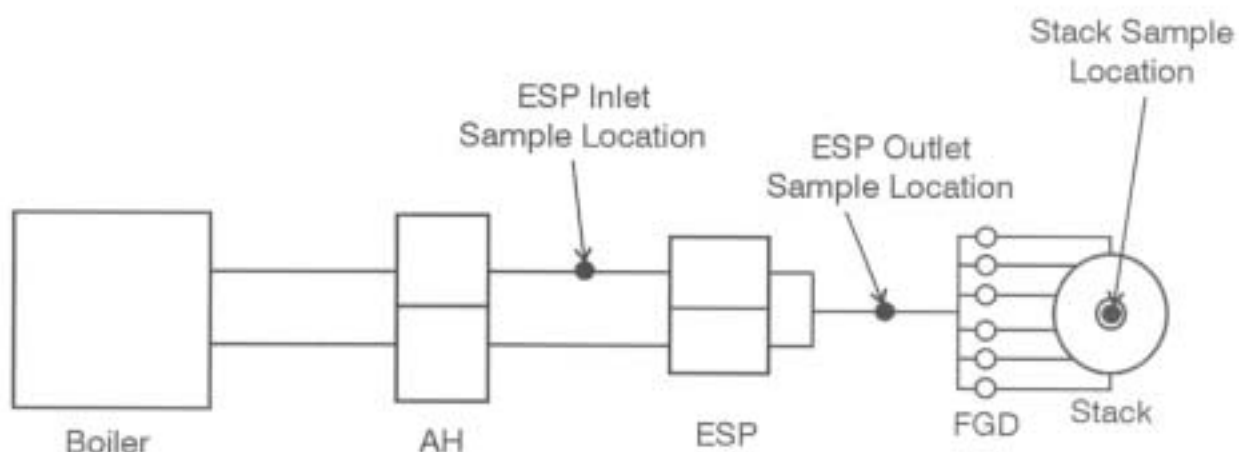
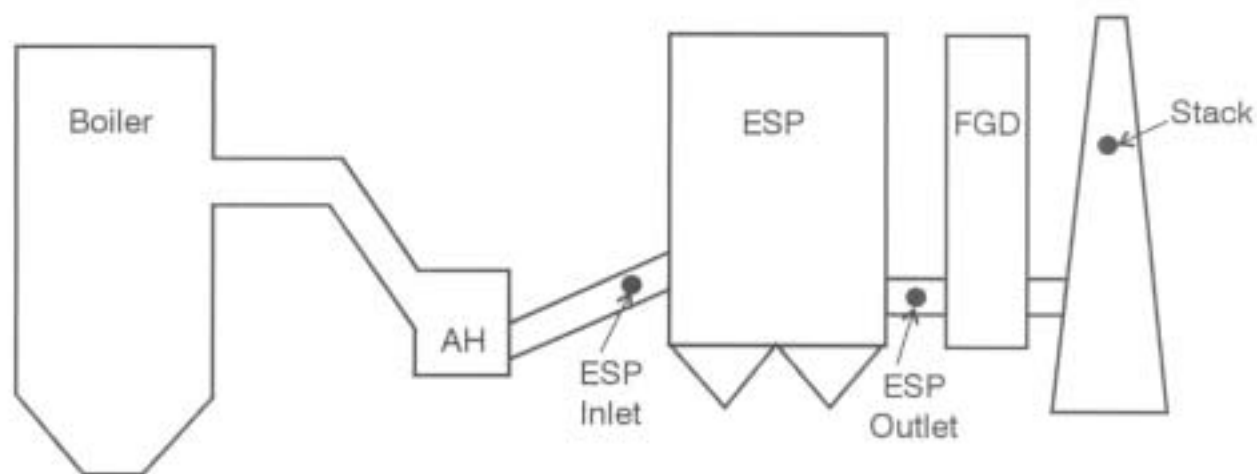
Site S5 fires a West Virginia high-sulfur bituminous coal. The unit with SCR has a plate configuration catalyst manufactured by Halder-Topsoe. The SCR unit had a space velocity of  $3700 \text{ hr}^{-1}$  and had operated for approximately 3 months prior to testing. Both the units tested operated ESPs for particulate control and wet FGDs to reduce  $\text{SO}_2$  emissions. Information about the configuration of the two units is presented below:

- Fuel type: West Virginia bituminous coal
- Boiler capacity: 684 MW
- Boiler type: wall-fired pc
- $\text{NO}_x$  control: SCR on one unit; low- $\text{NO}_x$  burners on both units
- Particulate control: ESP
- $\text{SO}_2$  control: magnesium-enhanced lime FGD

Schematics of the two units at Site S5, including sampling locations, are shown in Figures 4-1 and 4-2. As shown in the figures, the ESP configuration was slightly different. The unit without SCR had a second ESP in series.



**Figure 4-1**  
Schematic of Site S5 Showing Sample Locations for the Unit with the SCR from a Vertical and Horizontal Perspective



**Figure 4-2**  
Schematic of Site S5 Showing Sample Locations for the Unit with No SCR from a Vertical and Horizontal Perspective

## 4.2 Sampling Approach

### 4.2.1 Flue Gas Sample Streams

The flue gas Hg speciation was measured using the OH method at five locations for the unit with SCR and three locations for the unit without SCR. A test matrix, which identifies the location of flue gas measurements, is provided in Table 4-1. Where practical, OH measurements were conducted simultaneously across the various control devices in an effort to quantify the effect

**Table 4-1**  
**Sampling Test Matrix for Site S5**

Date		SCR In	SCR Out	ESP In	ESP Out	Stack	AH In	ESP In	SCR Out	SCR Out
Begin	End	OH	OH	OH	OH	OH	SO <sub>3</sub>	SO <sub>3</sub>	SO <sub>3</sub>	NH <sub>3</sub>
<i>With SCR</i>										
07/26/02	07/28/02				3					
08/15/02	08/23/02	3	5	3	5	2		3	3	3
<i>Without SCR</i>										
07/26/02	07/28/02				3					
08/13/02	08/23/02			3	4	3	2	2		

each had on Hg concentration and speciation. In addition to Hg, flue gas samples were collected to measure the total particulate loading and SO<sub>3</sub> concentrations. Additionally, NH<sub>3</sub> slip samples were collected from the unit with SCR to evaluate performance.

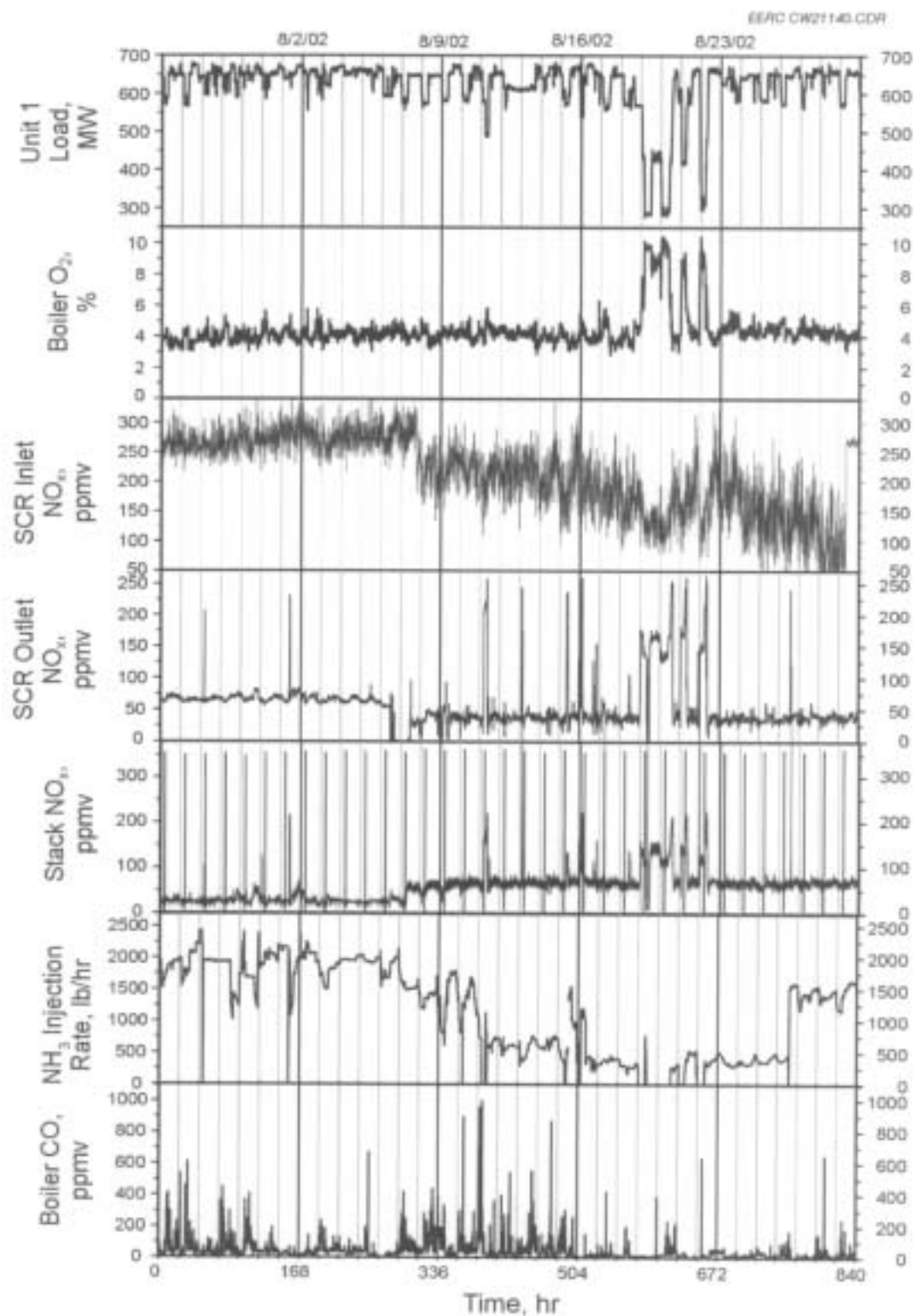
Longer-term Hg monitoring was conducted using Hg SCEMs (PSA) located at the ESP outlet (same as the FGD inlet) locations for both test units. These data provided semicontinuous Hg<sup>0</sup> and total gas-phase Hg concentrations for approximately 3 weeks.

#### 4.2.2 Other Sample Streams

Samples of coal and ESP hopper ash were collected from both test units in an effort to obtain representative operational data related to Hg speciation. These samples were analyzed for Hg and, along with the flue gas emission data, were used to qualitatively evaluate the fate of Hg throughout the units. Coal samples were collected daily throughout the test period from the coal feeder of both units. ESP hopper ash samples were collected from the first fields of the ESPs. Ash samples for the unit with SCR were obtained from both Sides A and B of the ESP; however, the sample collected from the unit without SCR was obtained from only Side A of the ESP. Plant personnel did not collect samples from the FGD system.

### 4.3 Process Operating Conditions

Plant operational data are presented in Figures 4-3 and 4-4 for the two test units. These figures summarize flue gas characteristics during the test program. Additionally, monthlong Hg SCEM data are included in these plots for comparison with plant operational data. Hg SCEM data will be discussed later in this report. In general, for the unit with SCR, plant load remained greater than 80% of full capacity, with the exception of a 35-hour period ~400 hours into the test and a few short reductions at night. These reduced load conditions did not have a significant impact on



**Figure 4-3**  
**Plant Operation Data for Site S5 for the Unit with the SCR**

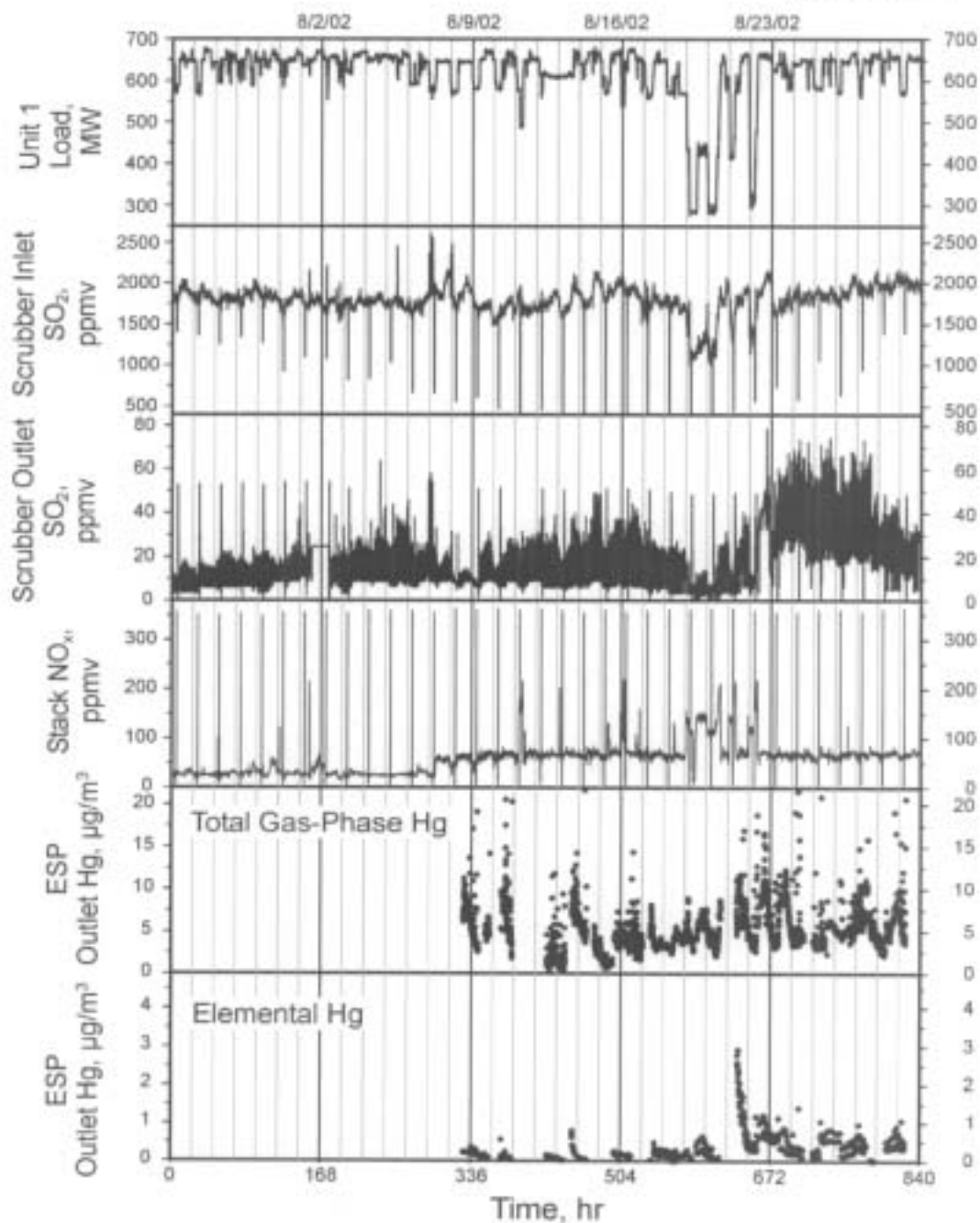
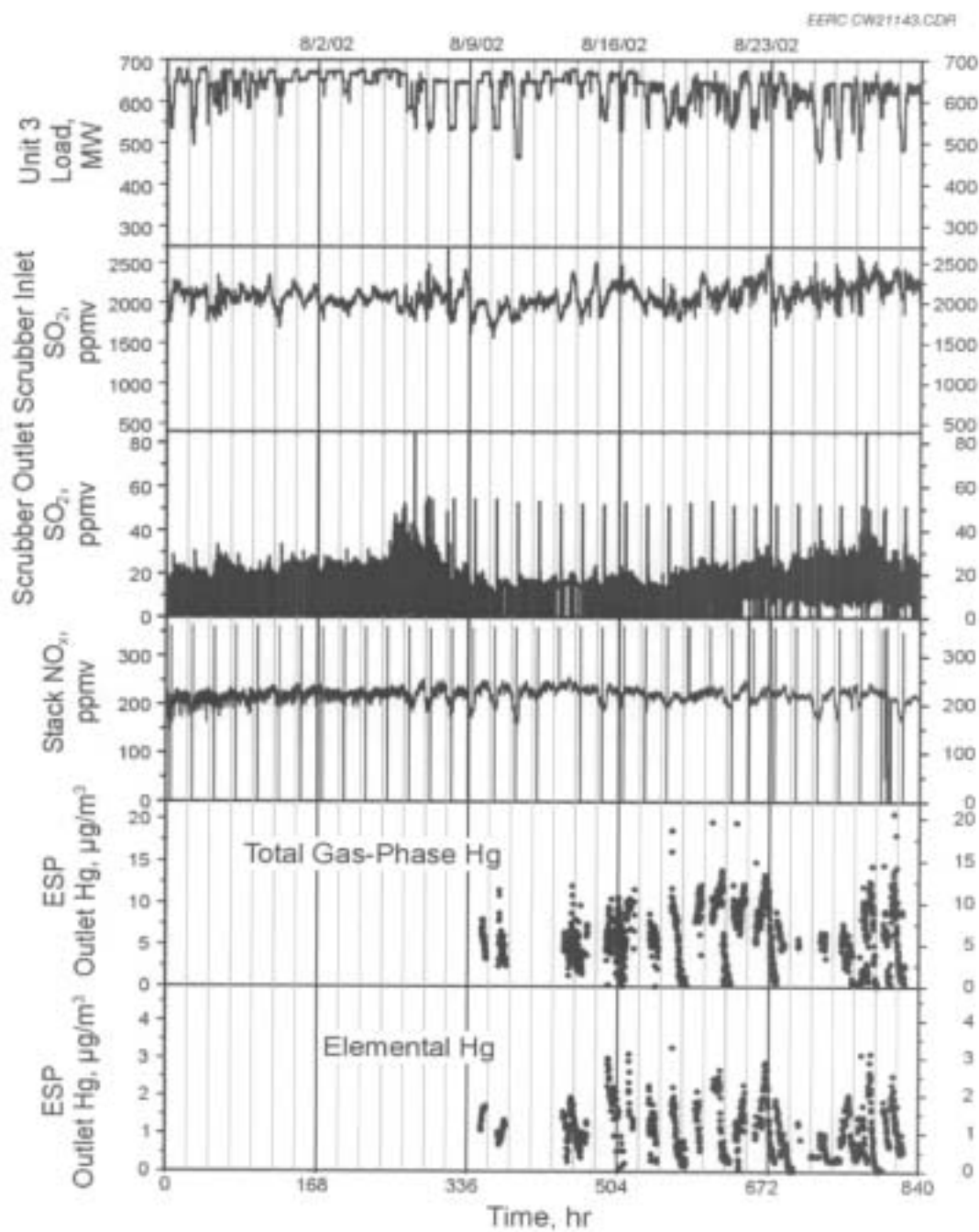
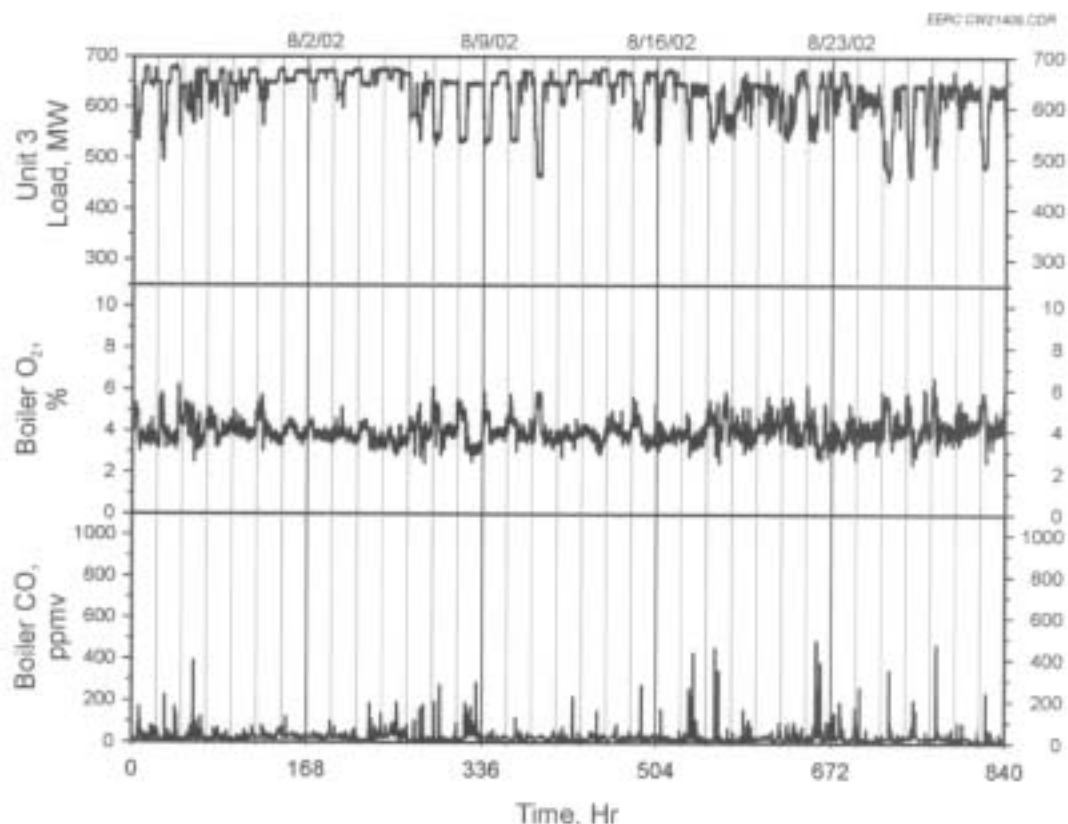


Figure 4-3 (continued)  
Plant Operation Data for Site S5 for the Unit with the SCR



**Figure 4-4**  
**Plant Operation Data for Site S5 for the Unit with No SCR**





**Figure 4-4 (continued)**  
**Plant Operation Data for Site S5 for the Unit with No SCR**

Hg as measured by the Hg SCEMs or OH method. The unit without SCR did not experience any significant load reductions below 80% of full capacity during the test program.

For the unit with SCR, the inlet  $\text{NO}_x$  concentration reduced noticeably beginning around 300 hours into the test from approximately 260 to less than 200 ppmv. In response to that reduction, the  $\text{NH}_3$  injection rate was reduced to maintain an SCR outlet  $\text{NO}_x$  concentration of approximately 50 ppm. Also, note at about 750 hours into the test, there is a substantial increase in the  $\text{NH}_3$  injection rate that corresponds to a spike in the SCR inlet  $\text{NO}_x$  concentration. Overall, an 80% reduction in  $\text{NO}_x$  was measured across the SCR unit.

Boiler CO for both units spiked intermittently from less than 50 to 400–800 ppm. However, there does not appear to be any correlation between elevated CO concentration and shifts in Hg concentration from either OH or Hg SCEM results.

A summary of auxiliary flue gas data, including percent  $\text{O}_2$  and percent  $\text{CO}_2$  for each sample location, is provided in Table 4-2. The complete data set is located in Appendix C, Table C-3. In general, the percent moisture,  $\text{CO}_2$ , and  $\text{O}_2$  were very consistent from day to day. However, there was air leakage across the SCR unit, air preheater, and wet FGD system that resulted in the  $\text{O}_2$  increasing from 4% at the boiler outlet to 7.8% at the stack. Dust-loading measurements collected at the ESP inlet and outlet location reflect a particulate removal efficiency of approximately 95% for both units based on an average of inlet and outlet dust loadings. Based on

**Table 4-2**  
**Auxiliary Flue Gas Data for Site S5\***

Date	Unit with SCR				Unit Without SCR			
	Moisture, %	Dust, gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %	Moisture, %	Dust, gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
SCR Inlet	10.7	3.5652	14.3	5.0				
SCR Outlet	9.1	3.4083	13.8	5.7				
ESP Inlet	8.9	1.6848	13.1	6.5	8.6	0.8287	13.6	6.1
ESP Outlet	8.7	0.0751	12.9	6.7	9.0	0.0453	12.9	6.7
Stack	13.1	0.0073	11.9	7.8	13.5	0.0063	12.7	7.0

\* Dust loadings were collected as part of the OH method using EPA Method 17 and, therefore, are not for compliance purposes.

discussions with plant personnel, the ESPs at S5 are not extremely efficient, which is reflected by these values.

## 4.4 Sampling Results

### 4.4.1 OH Flue Gas Mercury Results

The average Hg results from gas sampling are summarized in Table 4-3. The complete data sets are presented in Appendix B (Tables B-5 and B-6). Figure 4-5 shows a comparison of the data for the unit with the SCR and the unit without an SCR. As shown in Table 4-3, there is significant oxidation of Hg occurring across the SCR catalyst, from 43% Hg<sup>2+</sup> to 76% Hg<sup>2+</sup>. The percentage of Hg<sup>2+</sup> is further increased to 95% at the inlet to the ESP. It should be noted that the apparent increase in Hg<sup>0</sup> across the ESP for the unit with ESP is most likely due to reactivity with the fly ash across the filter of the OH method.

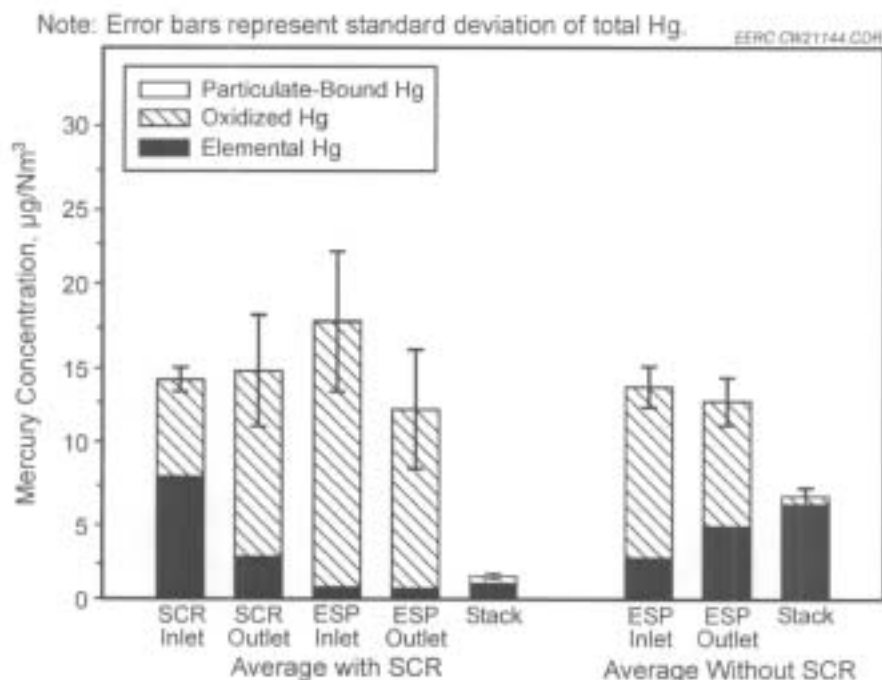
Comparing the ESP inlet Hg speciation results for the two units indicates that the percentage of Hg<sup>2+</sup> was 80% without SCR and 95% with SCR. However, as shown by the error bars in Figure 4-5, the OH data at this location were highly variable. If the ESP outlet data are used, the difference is from 63% to 94%. This is more in line with the overall Hg removal of 91% with SCR as compared to only 51% for the unit without SCR.

One objective for testing Site S5 was to evaluate the combined effect of an SCR unit and wet FGD system on Hg speciation and removal. For the unit without SCR, the measured Hg<sup>2+</sup> was 63% of the total Hg. However the Hg removal efficiency of the wet FGD system was only 51%. This is a result of the Hg<sup>0</sup> increasing from 4.7 to 6.1 µg/Nm<sup>3</sup> across the wet FGD system. With SCR, Hg<sup>2+</sup> is 94% of the total Hg, and the total Hg removal by the wet FGD system is 91%. There is still an increase in Hg<sup>0</sup> (0.7 to 1.0 µg/Nm<sup>3</sup>) across the wet FGD system, but it is small. It should be noted that the wet FGD system at Site S5 is a magnesium-enhanced lime system.

**Table 4-3**  
**Average and Percentage of Total OH Mercury Results for S5**

	Average, $\mu\text{g}/\text{Nm}^3$				Percentage of Total, %		
	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>T</sub>	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>
<i>Unit with SCR</i>							
SCR Inlet	0.09	6.1	7.8	14.0	1	43	56
SCR Outlet	0.02	10.8	3.3	14.3	0	76	24
ESP Inlet	0.07	16.8	0.8	17.6	0	95	5
ESP Outlet	0.05	11.3	0.7	12.1	0	94	6
Stack	0.02	0.4	1.0	1.5	1	28	72
Average total mercury removal = 91% <sup>a</sup>							
<i>Unit Without SCR</i>							
ESP Inlet	0.05	10.8	2.7	13.5	0	80	20
ESP Outlet	0.01	7.9	4.7	12.6	0	63	37
Stack	0.00	0.5	6.1	6.6	0	8	92
Average total mercury removal = 51% <sup>a</sup>							

<sup>a</sup> Average Hg removal is defined: (ESP inlet - stack)/ESP inlet.



**Figure 4-5**  
**Comparison of Mercury Speciation Results with the SCR and Without an SCR at Site S5**

Whether these mercury results would be consistent in the more common limestone forced-oxidation design is not known since the mechanism for reemission is not well understood. This is discussed in more detail in Section 6.4.

#### 4.4.2 Hg SCEM Results

Hg SCEMs were operated at the ESP outlet location for both units tested. In an effort to gather longer-term variability data, Hg SCEMs were operated nearly continuously for 23 days. The Hg SCEM data for the entire test are shown in Figures 4-6 and 4-7.

Significant variability of total gas-phase Hg was observed at the ESP outlet location of both units. The statistical analysis for the Hg SCEM data is shown in Table 4-4. Correlation between the Hg SCEM data and the OH method at Site S5 is not very good. Using the OH method, the average total gas-phase Hg was 9.1 and 9.9  $\mu\text{g}/\text{m}^3$  with and without SCR operating (dry at actual  $\text{O}_2$  levels). This compares to only 5.3 and 5.8  $\mu\text{g}/\text{m}^3$  as measured using the Hg SCEMs. There were significant problems associated with operating the Hg SCEMs at Site S5. It took a long time (over a week) to get the instruments operating, and once they began operating, there were substantial plugging problems of the sample lines and probe. In general, it is difficult to assess long-term variability of Hg concentration at S5. The abrupt shifts observed in the Hg SCEM data indicate that Hg concentrations were highly variable at S5. Complicating the Hg SCEM data interpretation further is a noticeable increase in Hg concentration following replacement of the probe or instrument filters.

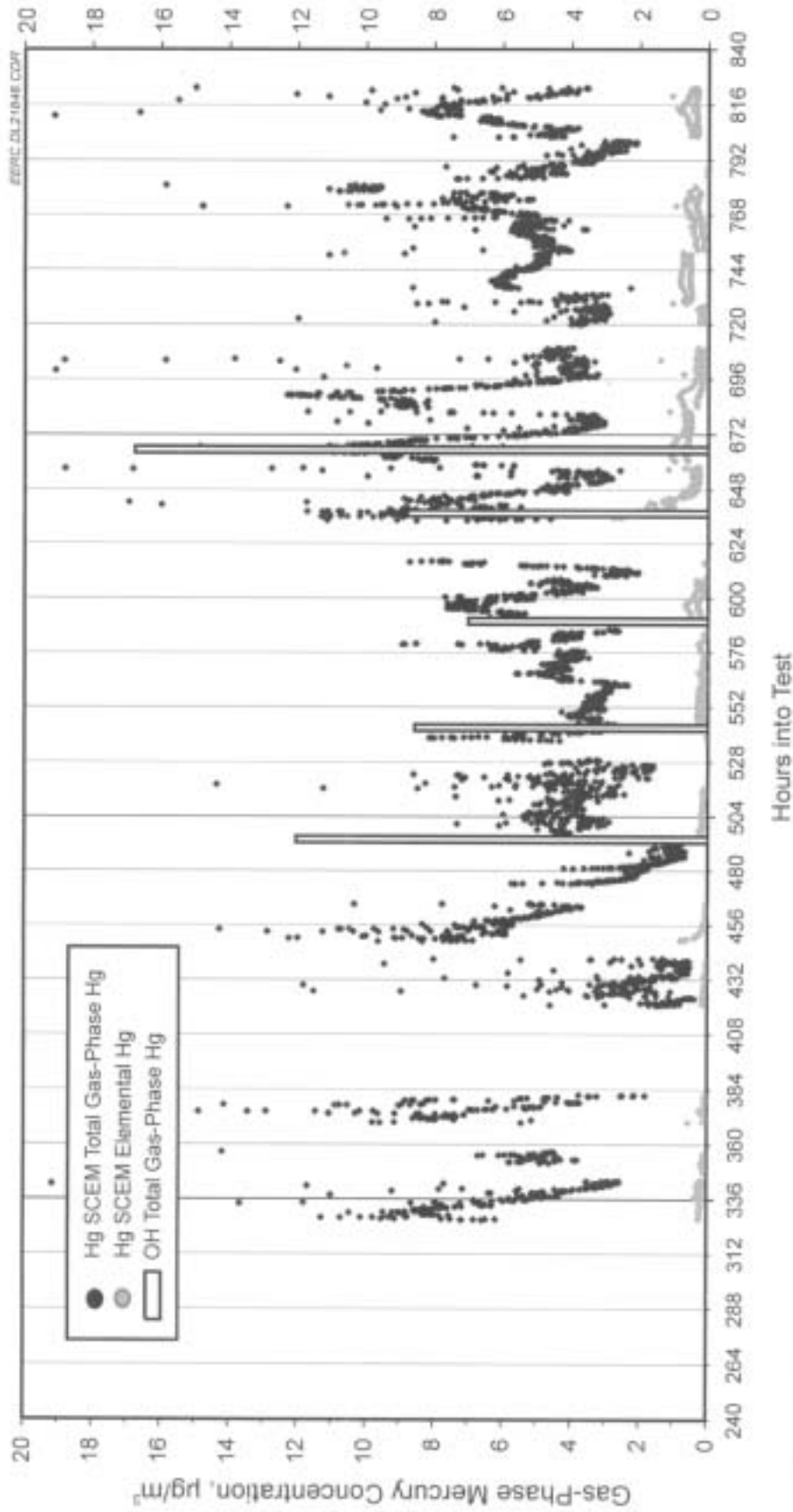


Figure 4-6  
Hg SCEM Results for Site S5 for the Unit with an SCR

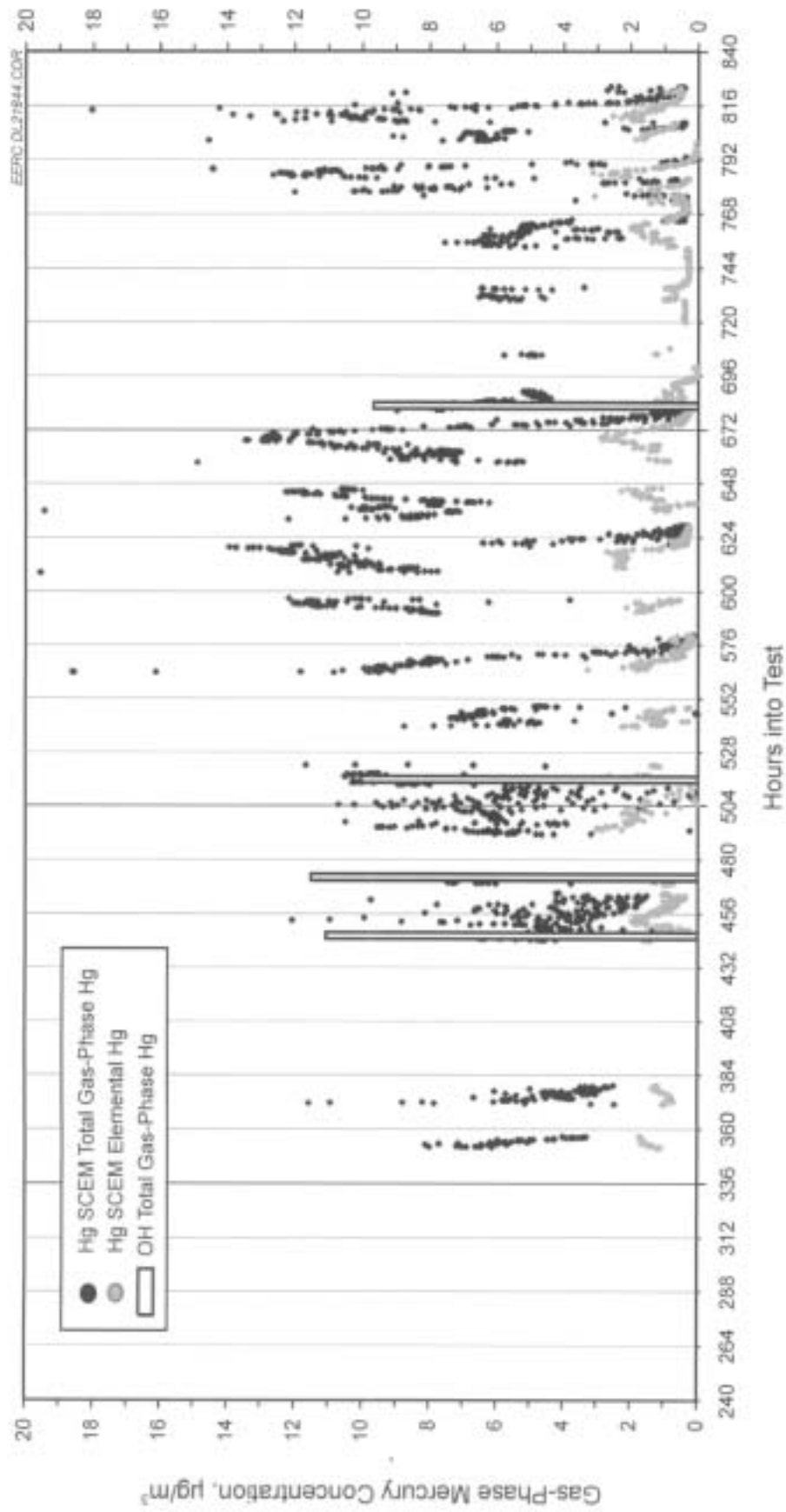


Figure 4-7  
Hg SCEM Results for Site S5 for the Unit with No SCR

**Table 4-4**  
**Statistical Variation of the Mercury with and Without the SCR in Service Based on the Hg**  
**SCEM Data for Site S5**

Mercury	Operation	Average, $\mu\text{g}/\text{m}^3$	Std. Dev., $\mu\text{g}/\text{m}^3$	Upper 90% CI, $\mu\text{g}/\text{m}^3$	Lower 90% CI, $\mu\text{g}/\text{m}^3$
Hg(total)	With SCR	5.3	3.9	11.6	0.0
Hg <sup>0</sup>	With SCR	0.2	0.4	0.9	0.0
Hg(total)	SCR bypassed	5.8	3.9	12.2	0.0
Hg <sup>0</sup>	SCR bypassed	0.8	0.7	1.5	0.0

#### **4.4.3 Coal Analysis Results**

Coal samples from S5 were analyzed for Hg and chloride. Both the coal Hg and chloride concentrations were very consistent. For six samples analyzed, the Hg and the chloride concentrations were  $0.13 \pm 0.013$  and  $472 \pm 28$  ppm, respectively. The analysis of the six coal samples is shown in Appendix B, Table B-7. Results of proximate and ultimate analyses for the coal are provided in Table 4-5.

**Table 4-5**  
**Coal Analysis for Site S5<sup>a</sup>**

Date		7/28/2002	8/5/2002	8/15/2002
Mercury	ppm (dry)	0.14	0.12	0.15
Chlorine	ppm (dry)	430	500	480
<b>Proximate Analysis</b>				
Moisture	wt%	5.1	4.8	3.9
Volatile Matter	wt%	37.7	38.3	38.7
Fixed Carbon	wt%	44.4	45.3	45.3
Ash	wt%	12.7	11.6	12.1
<b>Ultimate Analysis</b>				
Hydrogen	wt%	5.3	5.3	5.3
Carbon	wt%	69.4	69.8	71.5
Nitrogen	wt%	1.4	1.4	1.4
Sulfur	wt%	3.6	3.5	3.8
Oxygen	wt%	7.6	8.4	5.8
Heating Value	Btu/lb	11,918	12,164	12,278
F <sub>d</sub> Factor <sup>b</sup>	dscf/10 <sup>6</sup> Btu	10,416	10,219	10,460

<sup>a</sup> Except where noted, all results are on an as-received basis.

<sup>b</sup> As defined in EPA Method 19.

#### 4.4.4 ESP Ash Mercury Results

ESP hopper ash samples were collected daily throughout the test period from both test units. Ash analyses consisted of Hg and LOI determination and are presented in Table 4-6. In general, the Hg concentration in the ash was very low, <0.1 µg/g with or without SCR. The LOI for all samples analyzed was less than 7%. Based on these results, only a small amount of Hg was adsorbed by the ash and subsequently removed across the ESP. This is supported by OH results.



**Table 4-6**  
**Analysis of ESP Hopper Ash**

	Hg, $\mu\text{g/g}$	No. of Samples	LOI, %	No. of Samples
Unit with SCR	$0.094 \pm 0.041$	16	$5.21 \pm 1.27$	5
Unit Without SCR	$0.068 \pm 0.016$	21	$3.96 \pm 0.87$	6

#### 4.4.5 $\text{NH}_3$ Slip and $\text{SO}_3$ Flue Gas Results

A summary of the  $\text{NH}_3$  slip and  $\text{SO}_3$  results is provided in Table 4-7. The  $\text{NH}_3$  slip was less than 0.5 ppm for both samples, indicating an efficiently operating SCR. Based on the expected conversion of  $\text{SO}_2$  to  $\text{SO}_3$  that occurs across the SCR unit, it would be expected that the unit with SCR would have higher  $\text{SO}_3$  concentrations than the unit without SCR. Comparing the results at the ESP sampling location, this is indeed the case. However, the results at the SCR outlet are much lower than seems reasonable and the ESP inlet  $\text{SO}_3$  concentrations are actually higher. No clear cause has been identified that would explain these results.

**Table 4-7**  
**Flue Gas  $\text{SO}_3$  and  $\text{NH}_3$  Results for Site S5<sup>a</sup>**

$\text{SO}_3$ , ppm			$\text{NH}_3$ Slip, ppm
<i>Unit with SCR</i>			
Date	SCR Outlet	ESP Inlet	SCR Outlet
8/18/2002	1.93		
8/18/2002		5.28	0.29
8/22/2002	1.71	16.03	0.34
8/22/2002	1.76	18.30	
<i>Unit Without SCR</i>			
Date	AH Inlet	ESP Inlet	
8/14/2002	10.61	9.92	
8/15/2002	5.06		
8/15/2002		5.13	

<sup>a</sup> Dry and 3% oxygen.

## 4.5 Mercury Mass Balance

Average Hg concentration in the coal and  $F_d$  factors (Table 4-5) were used to estimate the Hg emission rate at the various sample locations. For the Hg associated with the ESP hopper ash, the  $F_d$  factors were based on the dust-loading measurements as well as the  $F_d$  factor. The results are shown in Table 4-8.

**Table 4-8**  
**Average Mercury Emission Factors for Site S5**

	lb Hg/10 <sup>12</sup> Btu				
	Coal	ESP Inlet	ESP Hopper Ash	ESP Outlet	Stack
Unit with SCR	10.8	13.4	0.2	9.2	1.1
Unit Without SCR	10.8	10.3	0.2	9.6	5.0

A Hg balance comparing the measured Hg in the flue gas at the ESP inlet location compared to the Hg generated by the coal is 124% with SCR and 95% for the test on the unit without SCR.

To determine the mass balance around the ESP the sum of the Hg associated with the ESP hopper ash plus the Hg in the flue gas at the ESP outlet must equal the Hg measured in the flue gas at the ESP inlet. The results of this balance for the units with and without SCR are 70%, and 95%. It should be noted that there was substantial variability in the Hg flue gas measurements. This is particularly true at the ESP inlet location where the standard deviation was 3.4 lb/10<sup>12</sup> Btu for the unit with SCR and 2.9 lb/10<sup>12</sup> Btu for the unit without SCR.

Unfortunately, the plant personnel did not provide FGD samples for analysis, and no plant data are available (gas flows, slurry feed rate, and blowdown) to estimate the Hg removal rates by the FGD. Therefore, it is not possible to do a Hg mass balance around the wet FGD system.

## 4.6 General Observations from S5

- There was an increase in Hg oxidation across the SCR catalyst. The percentage of Hg<sup>2+</sup> in the flue gas increased from 43% to 76%. At the ESP inlet and outlet location, the percentage of Hg<sup>2+</sup> was 95%.
- Comparing the Hg speciation results (at the ESP inlet location) with and without the SCR unit in service showed that the presence of SCR resulted in more Hg<sup>2+</sup>: 80% without SCR and 95% with SCR. There was substantial variability at the ESP inlet locations for both units. If the ESP outlet data are used, the difference was 63% to 94%.
- The overall Hg removal was greater with an SCR: 51% for the unit tested without SCR and 91% when SCR was in service.
- There was an increase in Hg<sup>0</sup> across the wet FGD system for both units. For the unit without SCR, the Hg<sup>0</sup> concentration increased from 4.7 µg/Nm<sup>3</sup> at the FGD inlet to 6.1 µg/Nm<sup>3</sup> at the outlet. The increase was less for the unit with SCR: 0.7 to 1.0 µg/Nm<sup>3</sup>.

- Hg removed by the ESP was low: an average of 0.2 lb Hg/10<sup>12</sup> Btu for the two units.

# 5

## SITE S6

Site S6 was selected for inclusion in the 2002 SCR testing to provide data associated with burning a compliance low-sulfur eastern bituminous coal. The primary tests were conducted on two of the four units at Site S6. On one of the units, SCR was operated for the entire testing period; however, on the other, SCR was bypassed for the majority of the test period. In addition, at Site S6, additional testing was done at the stack of a third unit (no SCR) as part of a separate test program. For comparison purposes, the results obtained at this unit are also presented in this report.

### 5.1 Site Description and Configuration

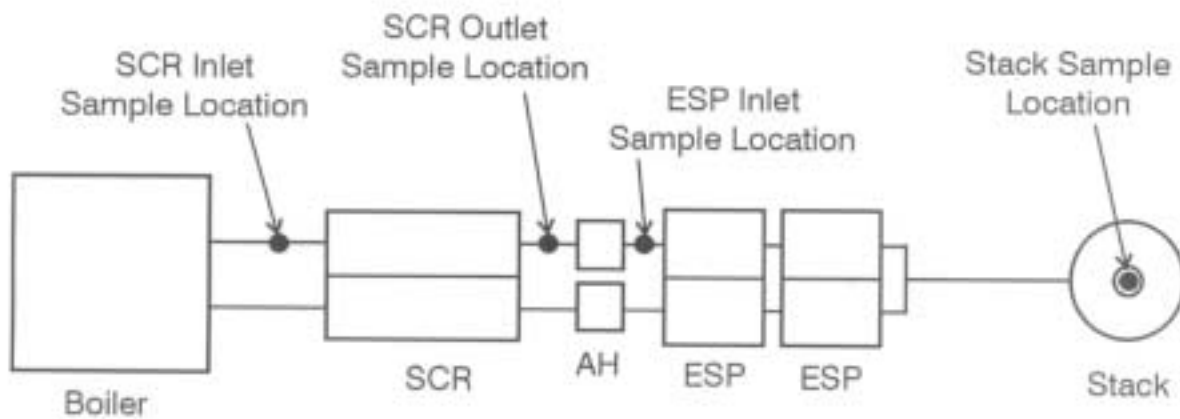
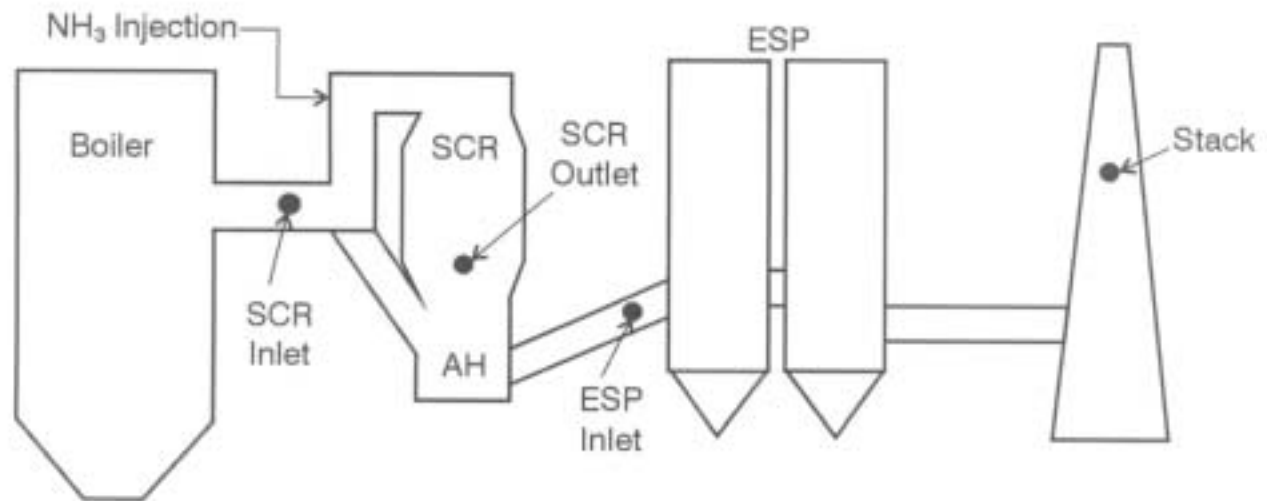
Site S6 operates four units consisting of two sets of similar configurations. Two of the four units have SCR units to reduce  $\text{NO}_x$ , and all four units have ESPs for particulate control. The SCR catalysts at Site S6 are a honeycomb type and manufactured by Cormetech. The SCR unit has a space velocity  $3800 \text{ hr}^{-1}$ . The SCR units have been operating for two ozone seasons. In between the two seasons, one layer of catalyst was changed. Specifications of the Site S6 units are presented in Table 5-1.

**Table 5-1**  
**Specifications of Site S6 Units<sup>a</sup>**

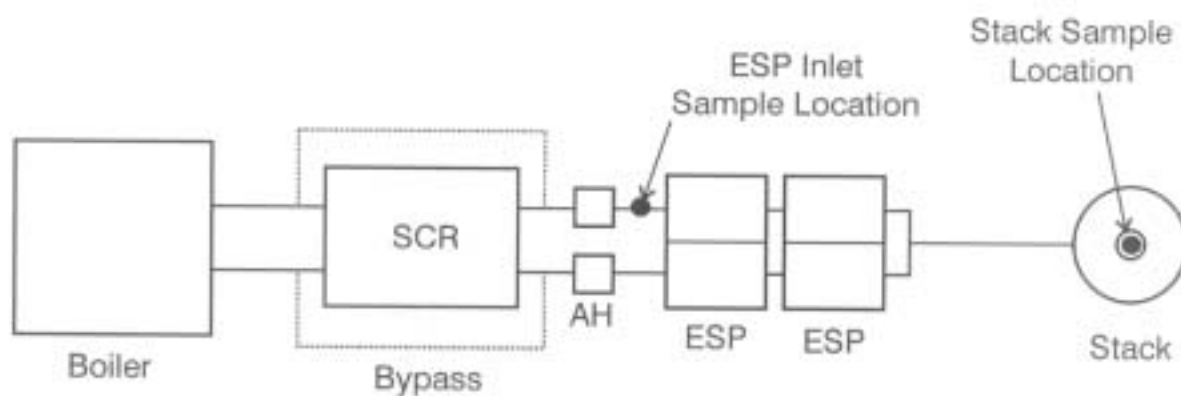
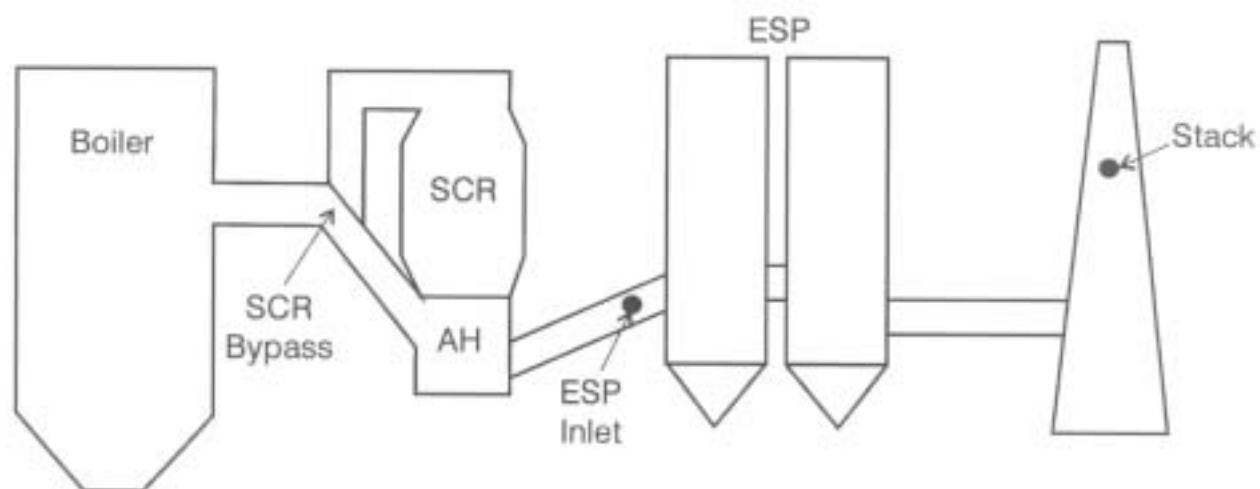
Specification	Unit 1	Unit 2	Unit 4
Fuel Type	KY and WV eastern bituminous coal	KY and WV eastern bituminous coal	KY and WV eastern bituminous coal
Boiler Capacity	700 MW	700 MW	900 MW
Boiler Type	tangentially fired	tangentially fired	tangentially fired
Low- $\text{NO}_x$ Burners	Yes	Yes	Yes
SCR	Yes	Operated in bypass mode	No
Particulate Control	ESP	ESP	ESP
$\text{SO}_2$	Low-sulfur compliance coal	Low-sulfur compliance coal	Low-sulfur compliance coal

<sup>a</sup> Site S6 has four units. Unit 3 (no testing was done at this time) is the same as Unit 4.

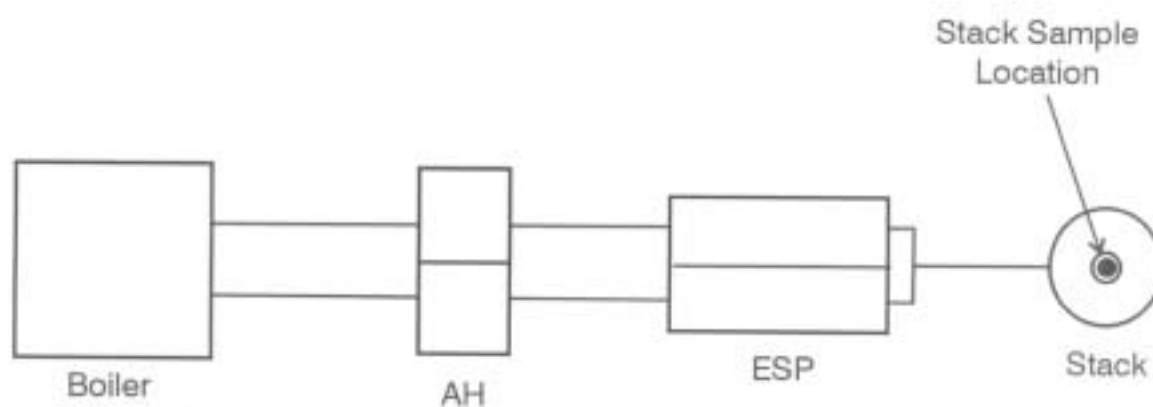
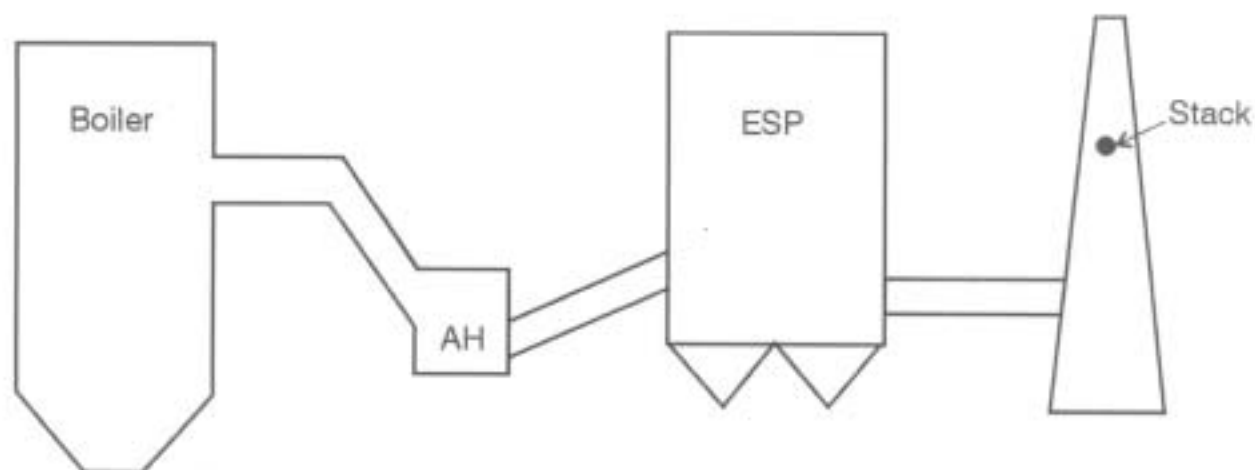
Schematics of the three test units at Site S6, including sampling locations, are shown in Figures 5-1 through 5-3.



**Figure 5-1**  
Schematic of Site S6 Showing Sample Locations for Unit 1 with the SCR in Service from a Vertical and Horizontal Perspective



**Figure 5-2**  
**Schematic of Site S6 Showing Sample Locations for Unit 2 with the SCR Bypassed from a Vertical and Horizontal Perspective**



**Figure 5-3**  
Schematic of Site S6 Showing Sample Locations for Unit 4 with No SCR from a Vertical and Horizontal Perspective

## 5.2 Sampling Approach

As stated previously, sampling at S6 was primarily conducted on two units (1 and 2) both with SCR, but the SCR unit was bypassed on Unit 2. Data collected from these similar units provided a comparison of speciated Hg emissions from SCR and no-SCR operation.

### 5.2.1 Flue Gas Sample Streams

The flue gas Hg speciation was measured using the OH method at four locations for Unit 1 (SCR) and two locations for Unit 2 (SCR bypassed). A test matrix, which identifies the location of flue gas measurements, is provided in Table 5-2. Where practical, OH measurements were conducted simultaneously across the various control devices in an effort to quantify the effect each had on Hg concentration and speciation. In addition to Hg, flue gas samples were collected to measure the total particulate loading and SO<sub>3</sub> concentrations. Additionally, NH<sub>3</sub> slip samples were collected from Unit 1 (SCR) to evaluate performance.

**Table 5-2**  
**Sampling Test Matrix for Site S6**

Date		SCR In	SCR Out	ESP In	Stack	SCR Out	SCR Out	ESP In
Begin	End	OH	OH	OH	OH	NH <sub>3</sub>	SO <sub>3</sub>	SO <sub>3</sub>
<i>Unit 1 (SCR)</i>								
09/22/02	09/26/02	4	4	4	5	2	2	2
10/08/02	10/18/02				7			
<i>Unit with SCR (Unit 2)</i>								
09/22/02	09/25/02				3			
<i>Unit 2 (SCR bypassed)</i>								
10/08/02	10/18/02			2	7		2	2
<i>Unit 4 (no SCR) – Plume Study</i>								
10/08/02	10/18/02				7			

Longer-term Hg monitoring was conducted using Hg SCEMs (PSA) located at the stack locations for each of the test units. These data provided semicontinuous Hg<sup>0</sup> and total gas-phase Hg concentrations for approximately 3 weeks.

### 5.2.2 Other Sample Streams

Samples of coal and ESP hopper ash were collected daily from the test units in an effort to obtain representative operational data related to Hg speciation. These samples were analyzed for Hg and, along with the flue gas emission data, were used to qualitatively evaluate the fate of Hg throughout the units. Daily coal samples were collected as composites from the different coal feeders. ESP hopper ash samples were collected from the first fields of the ESPs.

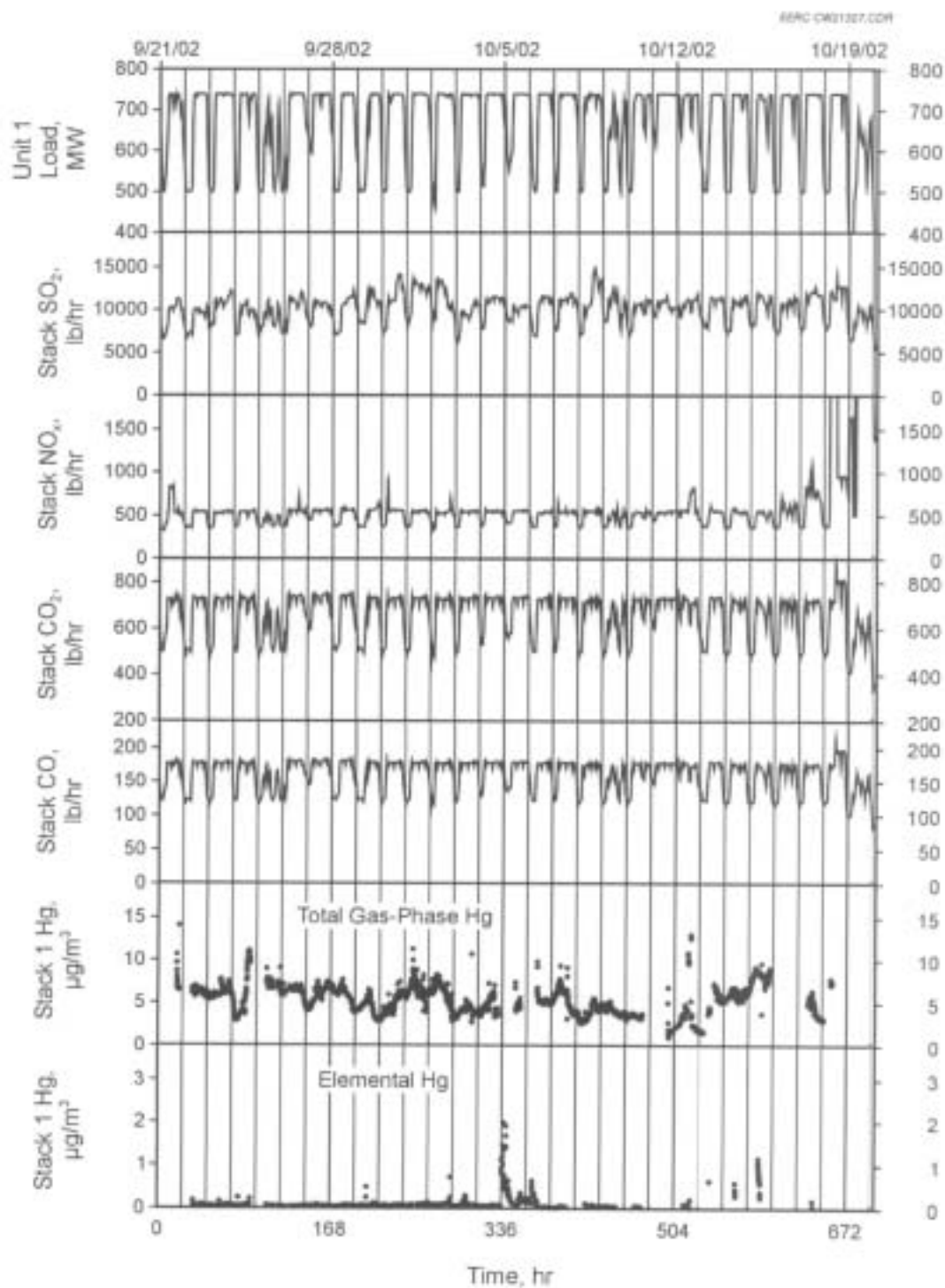


### **5.2.3 Process Operating Conditions**

Plant operational data are presented in Figures 5-4 through 5-6 for the test units. These figures summarize flue gas characteristics during the test program. Additionally, monthlong Hg SCEM data are included in these plots for comparison with plant operational data. Hg SCEM data will be discussed later in this report.

In general, during the day, the plant load at the two primary test units (Units 1 and 2) was near full load and would drop at night. However, at Unit 4 (no SCR), the plant data showed a significant load reduction at about 120 hours into the test.

A summary of auxiliary flue gas data, including percent O<sub>2</sub> and percent CO<sub>2</sub> for each sample location, is provided in Table 5-3 (the complete data set is in Table C-3 in Appendix C). In general, the percent moisture, CO<sub>2</sub>, and O<sub>2</sub> were very consistent from day to day. However, there was some air leakage across the air preheater that resulted in the O<sub>2</sub> increasing from 4.1% at the SCR inlet to 6.5% at the stack for Unit 1 (SCR). The air leakage was about the same for Unit 2 (SCR bypassed). Dust-loading measurements collected at the ESP inlet and outlet location reflect a particulate removal efficiency of >99% for both units based on an average of inlet and outlet dust loadings.



**Figure 5-4**  
**Plant Operation Data for Site S6 for Unit 1 with the SCR in Service**

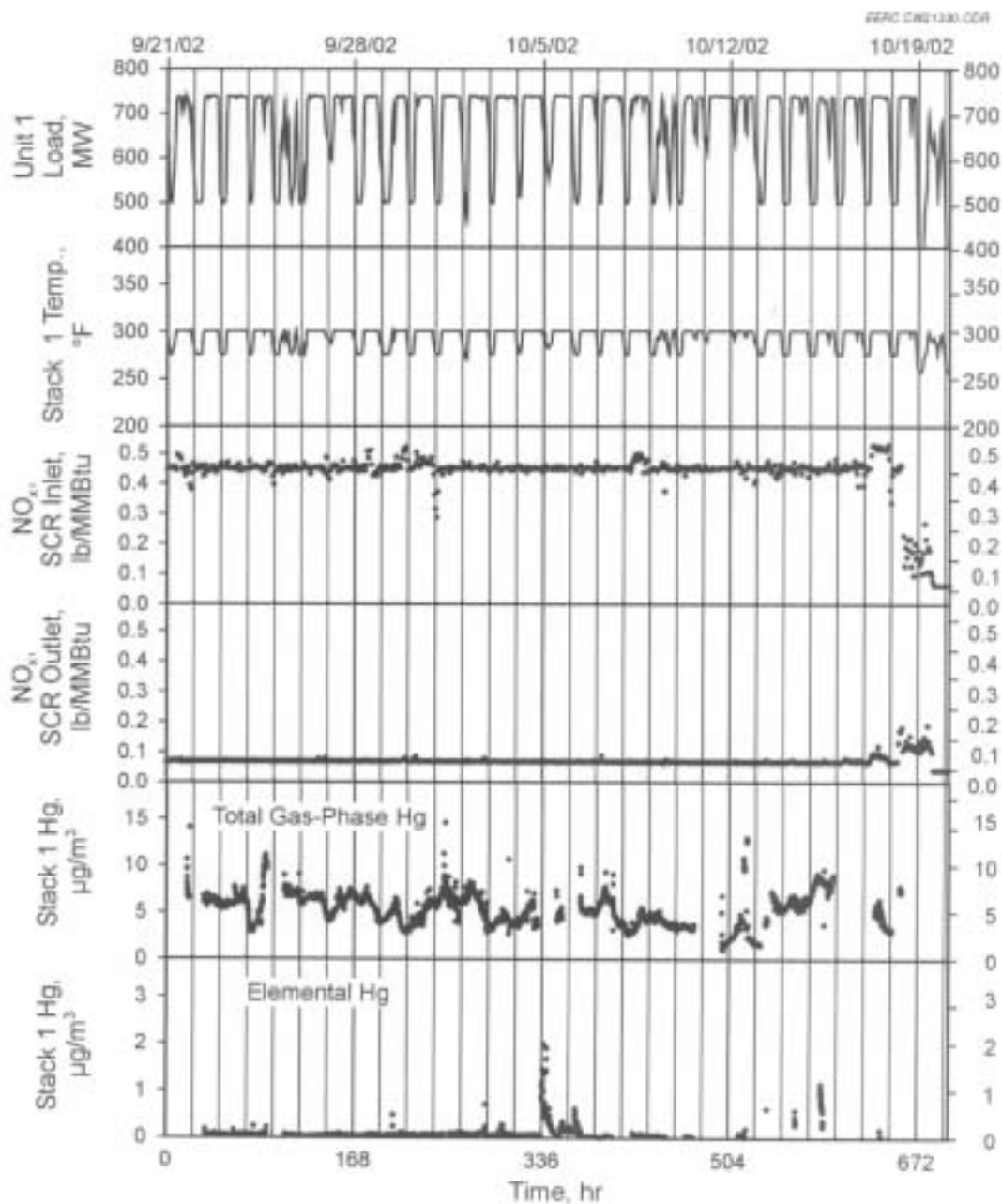
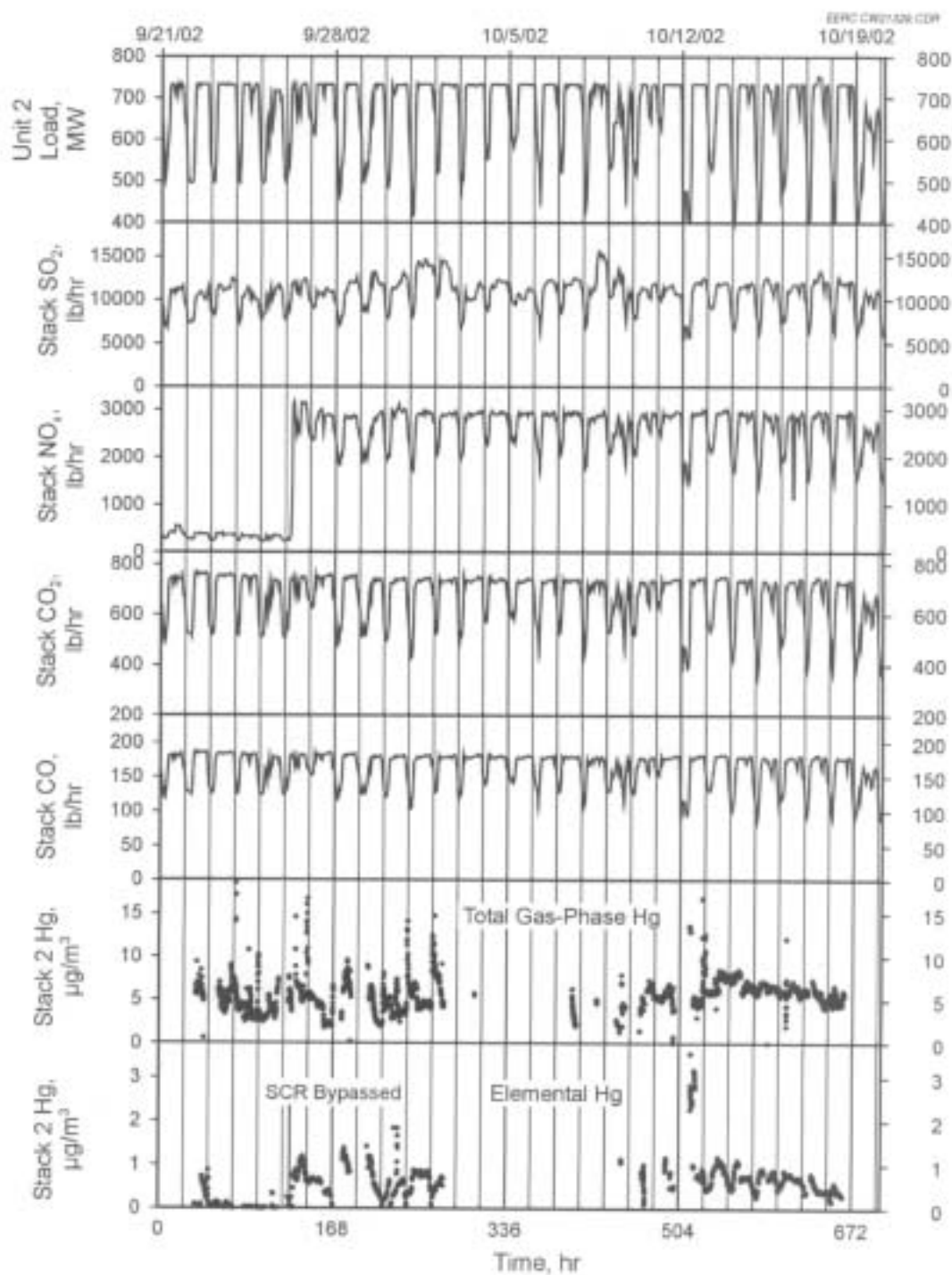
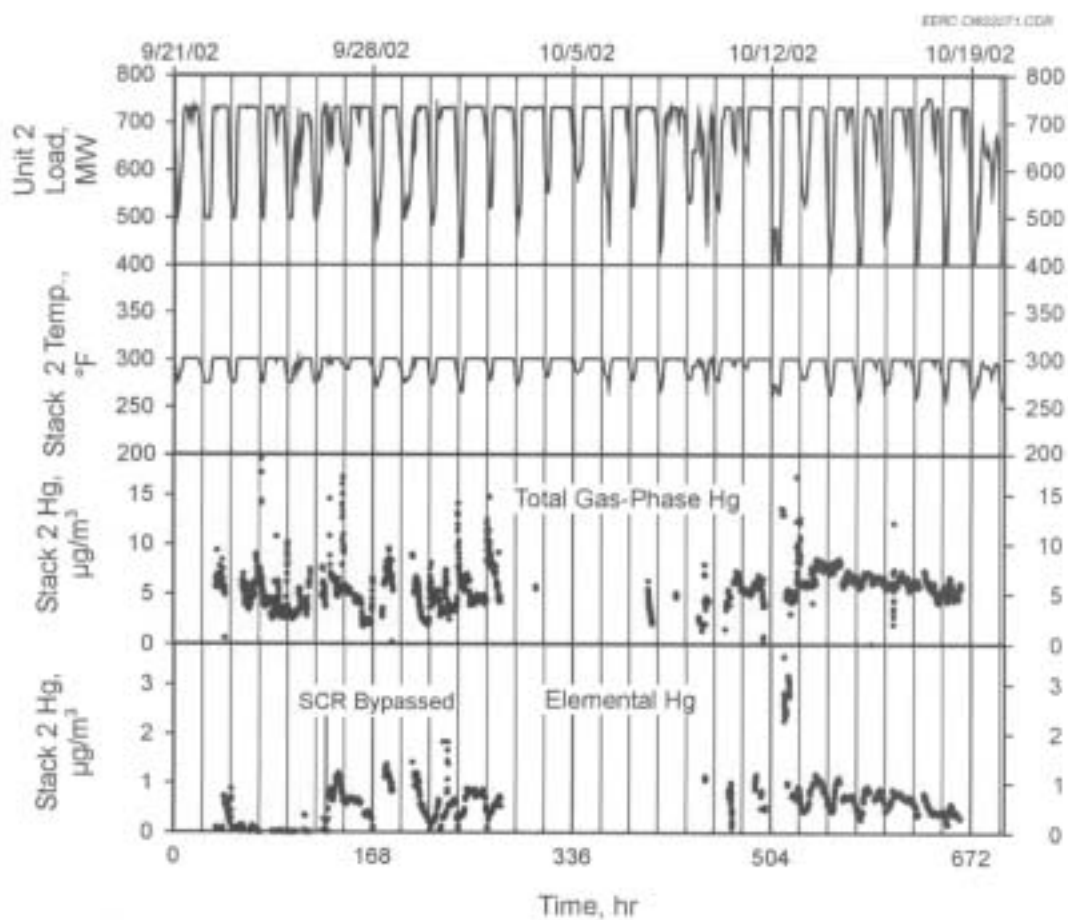


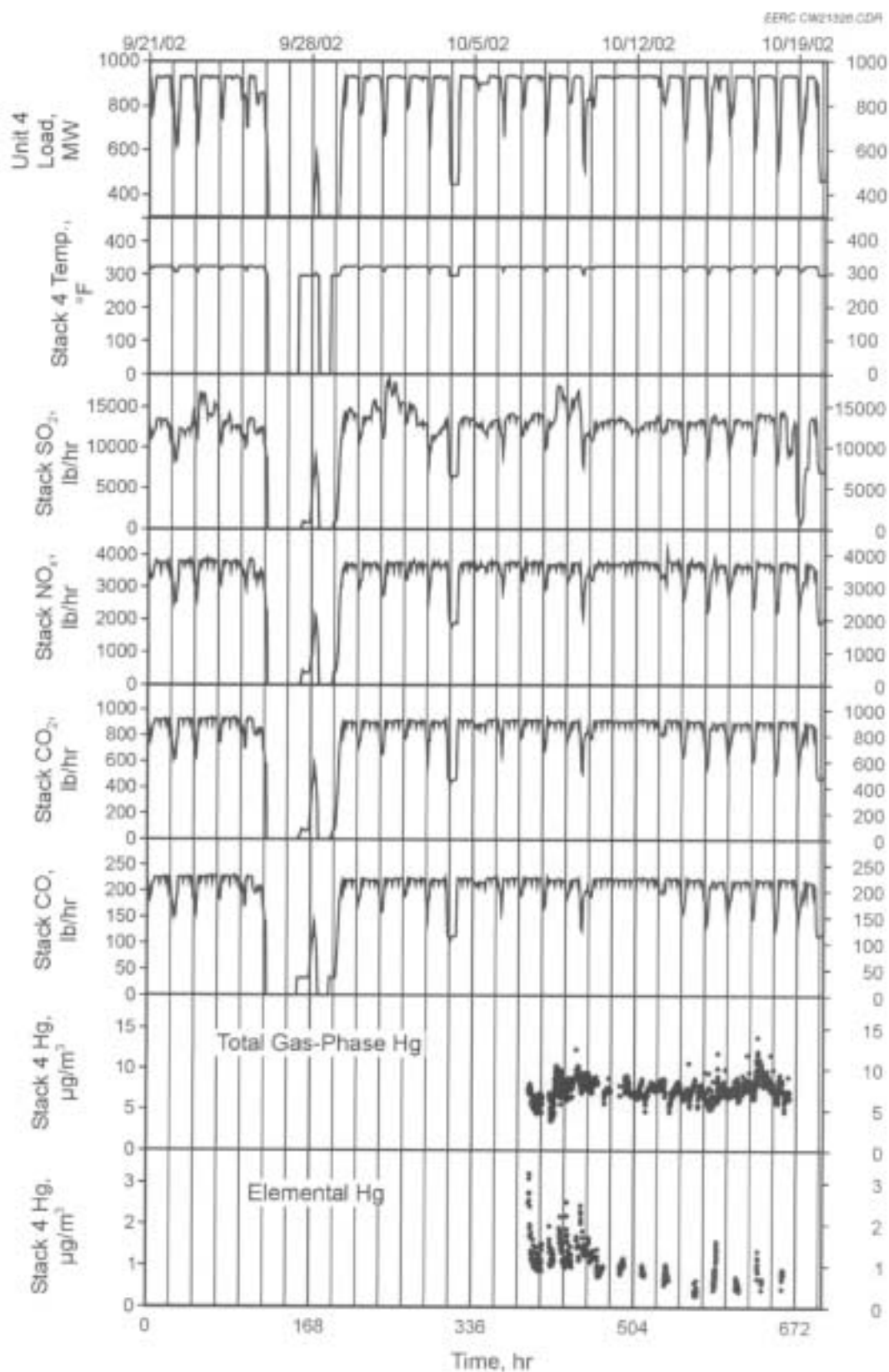
Figure 5-4 (continued)  
Plant Operation Data for Site S6 for Unit 1 with the SCR in Service



**Figure 5-5**  
**Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed**



**Figure 5-5 (continued)**  
**Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed**



**Figure 5-6**  
**Plant Operation Data for Site S5 for Unit 4 with No SCR**

**Table 5-3**  
**Auxiliary Flue Gas Data for Site S6**

	Moisture %	Dust,* gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>Unit 1 (SCR)</i>				
SCR Inlet	9.0	3.7306	14.7	4.1
SCR Outlet	8.7	4.1673	15.2	4.7
ESP Inlet	8.9	2.7321	13.8	5.0
Stack	9.3	0.0165	13.1	6.5
<i>Unit 2 (SCR bypassed)</i>				
ESP Inlet	8.3	4.2279	15.4	3.7
Stack	7.8	0.0150	13.2	6.4
<i>Unit 4 (no SCR)</i>				
Stack	7.8	0.0388	14.5	4.9

\* Dust loadings were collected as part of the OH method using EPA Method 17 and, therefore, are not for compliance purposes.

## 5.3 Sampling Results

### 5.3.1 OH Flue Gas Mercury Results

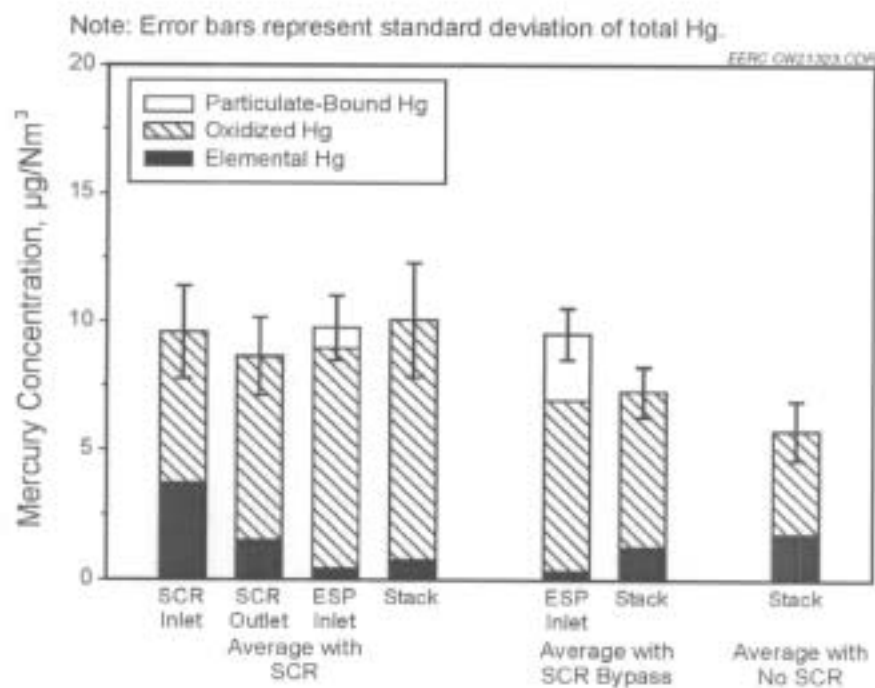
Average Hg results for flue gas sampling at Site S6 are presented in Table 5-4. The complete results are presented in Appendix B (Tables B-8 and B-9). As shown in Table 5-4, there is an increase in the concentration of Hg<sup>2+</sup> across the SCR catalyst from 60% to 82% Hg<sup>2+</sup>. There is only a slight additional increase to 87% at the ESP inlet location (this is within the variation of the data).

Comparing the ESP inlet Hg speciation results for Unit 1 (SCR) and Unit 2 (SCR bypassed) shows that the percentage of Hg<sup>2+</sup> was 69% with SCR bypassed and 87% with SCR. However, there was essentially no Hg removal across the ESP for either unit. A direct comparison including the error bars associated with the total Hg concentration for all three units is shown in Figure 5-7.

**Table 5-4**  
**Average and Percentage of Total OH Mercury Results for S6<sup>a</sup>**

	Average, $\mu\text{g}/\text{Nm}^3$				Percent of Total, %		
	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>
<i>Unit 1 (SCR)</i>							
SCR Inlet	0.04	5.8	3.8	9.6	0	60	40
SCR Outlet	0.03	7.1	1.5	8.6	0	82	18
ESP Inlet	0.80	8.5	0.5	9.8	8	87	5
Stack	0.00	9.3	0.8	10.1	0	92	8
<i>Unit 2 (SCR bypassed)</i>							
ESP Inlet	2.59	6.6	0.4	9.5	27	69	4
Stack	0.01	6.0	1.3	7.3	0	82	18
<i>Unit 4 (no SCR)</i>							
Stack	0.01	4.0	1.8	5.8	0	69	31

<sup>a</sup> All mercury results are on a dry basis corrected to 3% O<sub>2</sub>.



**Figure 5-7**  
**Comparison of Mercury Speciation Results for the Three Test Units**



### 5.3.2 Hg SCEM Results

Hg SCEMs were operated at the stack location of the three units tested. The Hg SCEMs were operated nearly continuously for a month. A summary of Hg SCEM data plotted over the entire test period for the three units is provided in Figures 5-8 through 5-10. The statistical average Hg SCEMs results are shown in Table 5-5. For Unit 1 (SCR), the Hg SCEM data averaged  $5.2 \mu\text{g}/\text{m}^3$  with 90% of the data falling between 2 and  $8 \mu\text{g}/\text{m}^3$ . For Unit 2 (SCR bypassed), the average Hg SCEM result was  $5.7 \mu\text{g}/\text{m}^3$ , with 90% of the data points falling within 1.3 and  $10.1 \mu\text{g}/\text{m}^3$ . For Unit 4 (no SCR), the Hg SCEM data averaged  $7.5 \mu\text{g}/\text{m}^3$  with 90% of the data points falling between 5.9 and  $9.1 \mu\text{g}/\text{m}^3$ . Although there is some difference between the OH data and the Hg SCEM averages, the results are within the statistical variability of the data.

The variability of the  $\text{Hg}^{2+}$  is shown in Figures 5-11 and 5-12. As can be seen, there appears to be a decrease in the percentage of  $\text{Hg}^{2+}$ , and there was more variability when SCR was bypassed. However, as was shown by the OH method, the percentage of  $\text{Hg}^{2+}$  at the stack was high (>90%) both with and without SCR.

At about 125 hours into the test (see Figure 5-5), there does appear to be a small increase in  $\text{Hg}^0$  concentration that corresponds with SCR being bypassed. Figure 5-13 presents the Hg SCEM data during this time period.

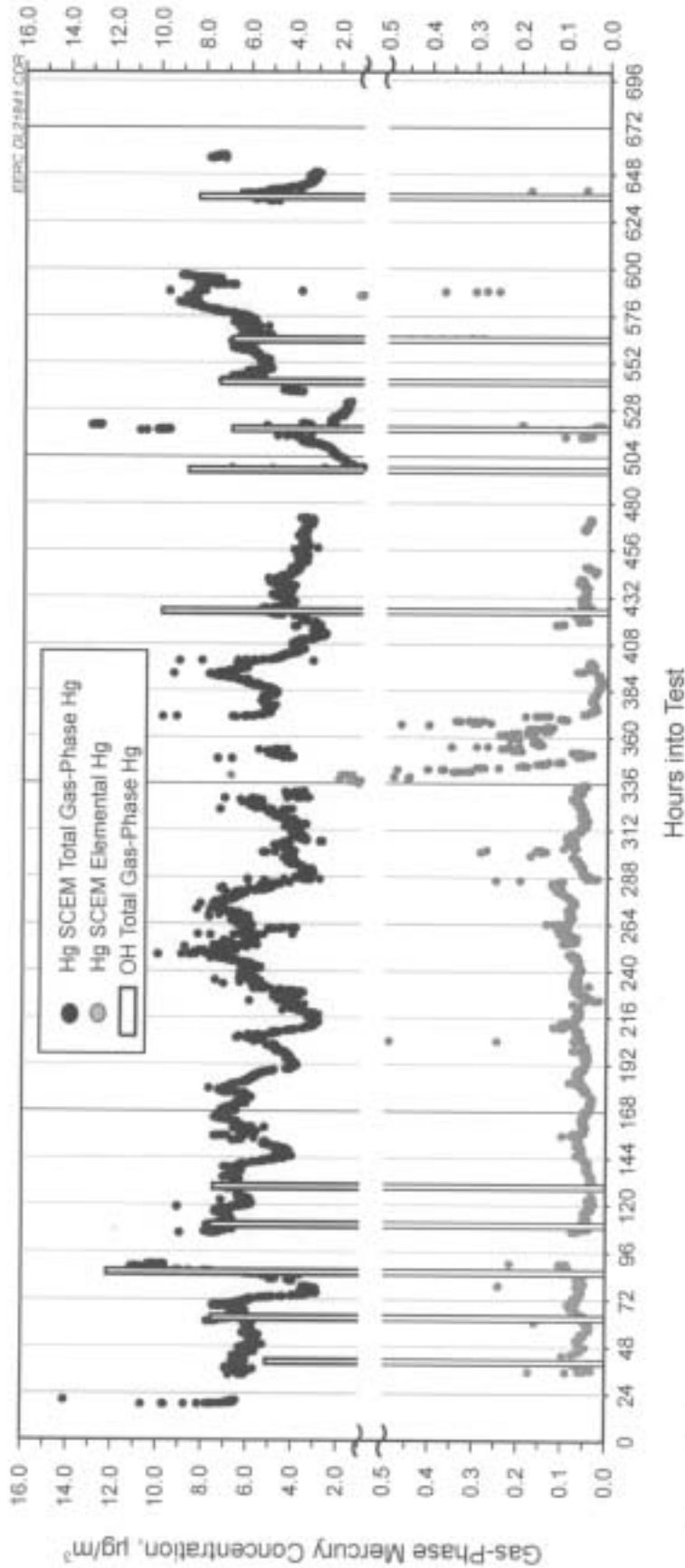


Figure 5-8  
Hg SCEM Results for Site S6 for Unit 1 with the SCR in Service

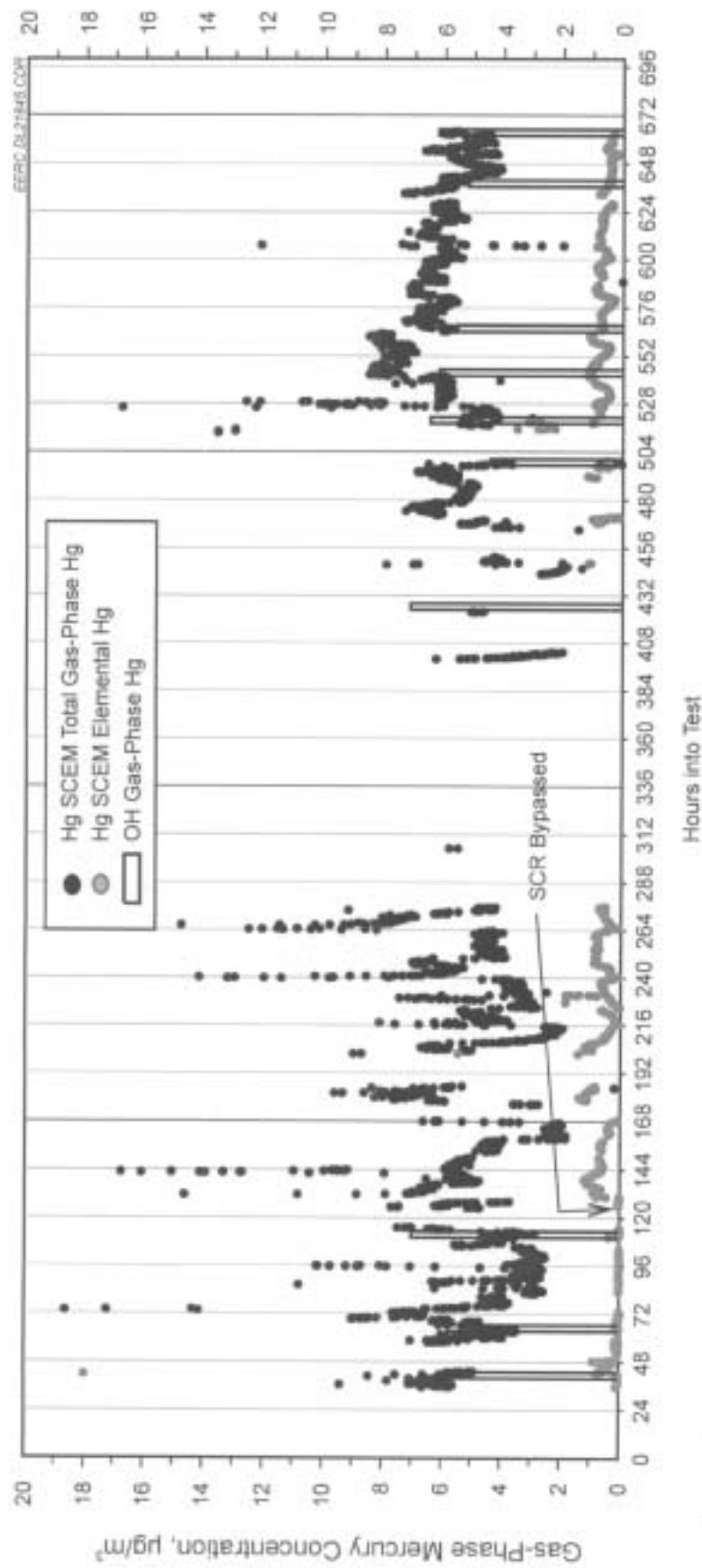


Figure 5-9  
Hg SCEM Results for Site S6 for Unit 2 with the SCR Bypassed

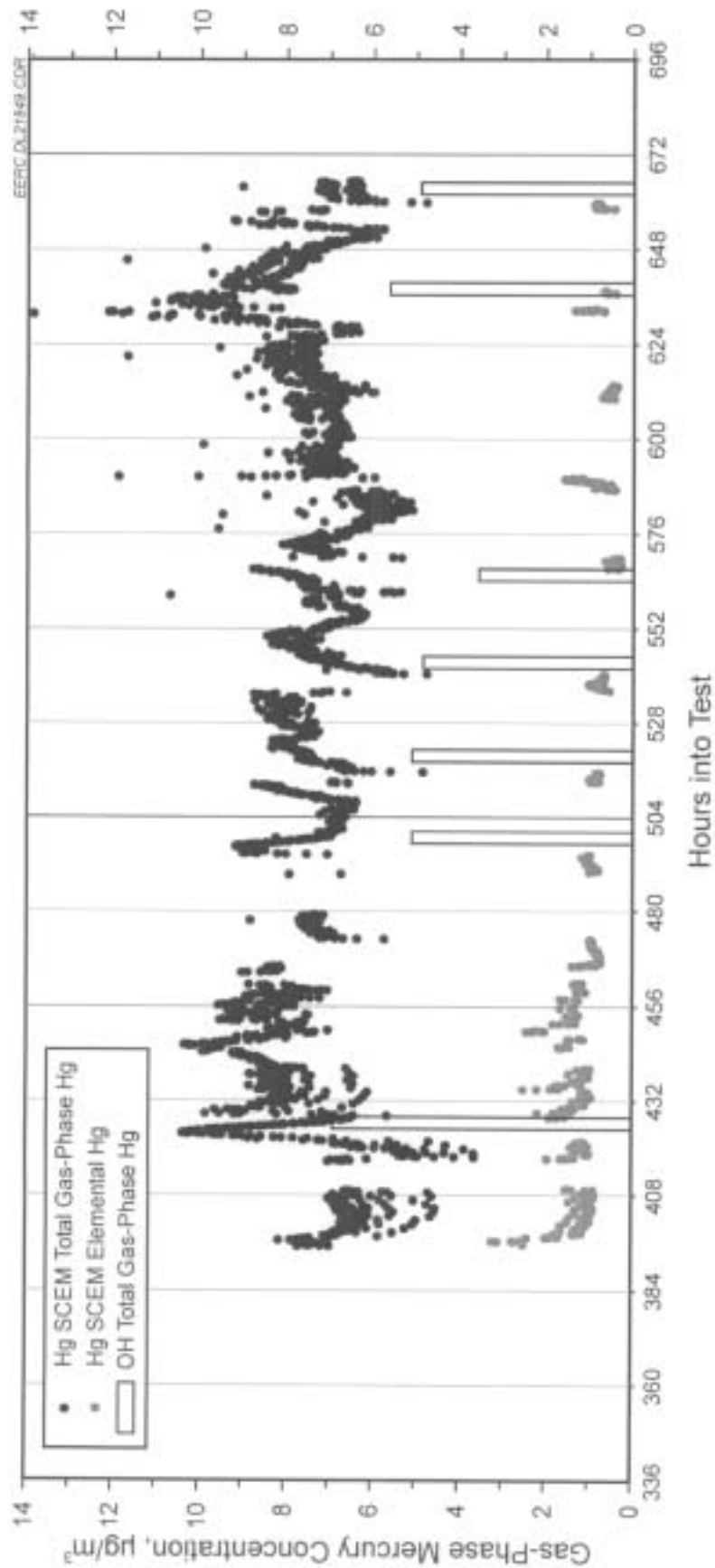
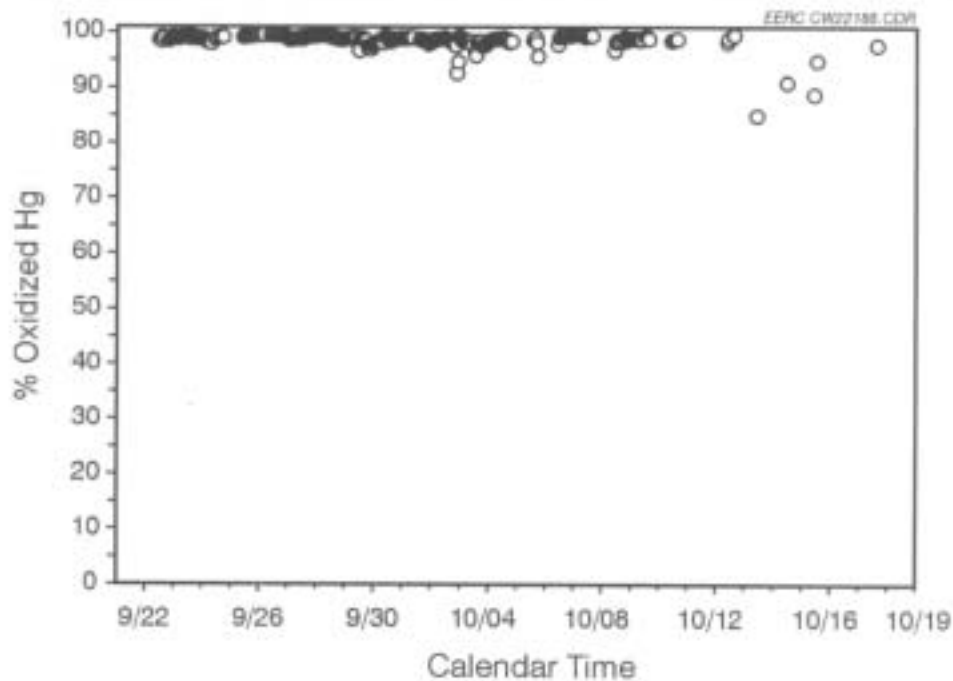


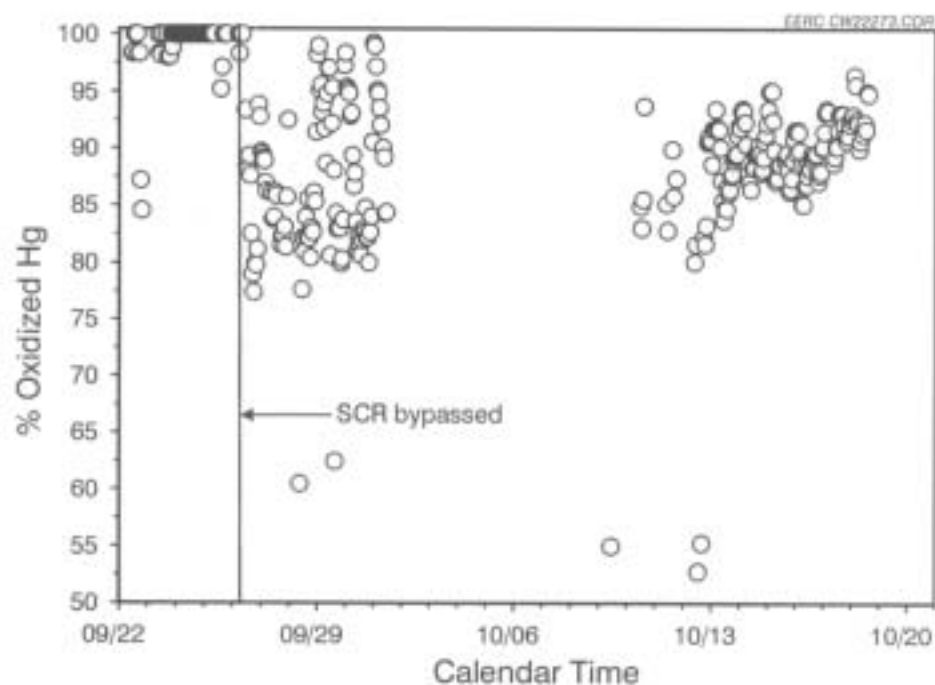
Figure 5-10  
Hg SCEM Results for Site S6 for Unit 4 with No SCR

**Table 5-5**  
**Statistical Variation of the Mercury Results Based on the Hg SCEM Data for Site S6**

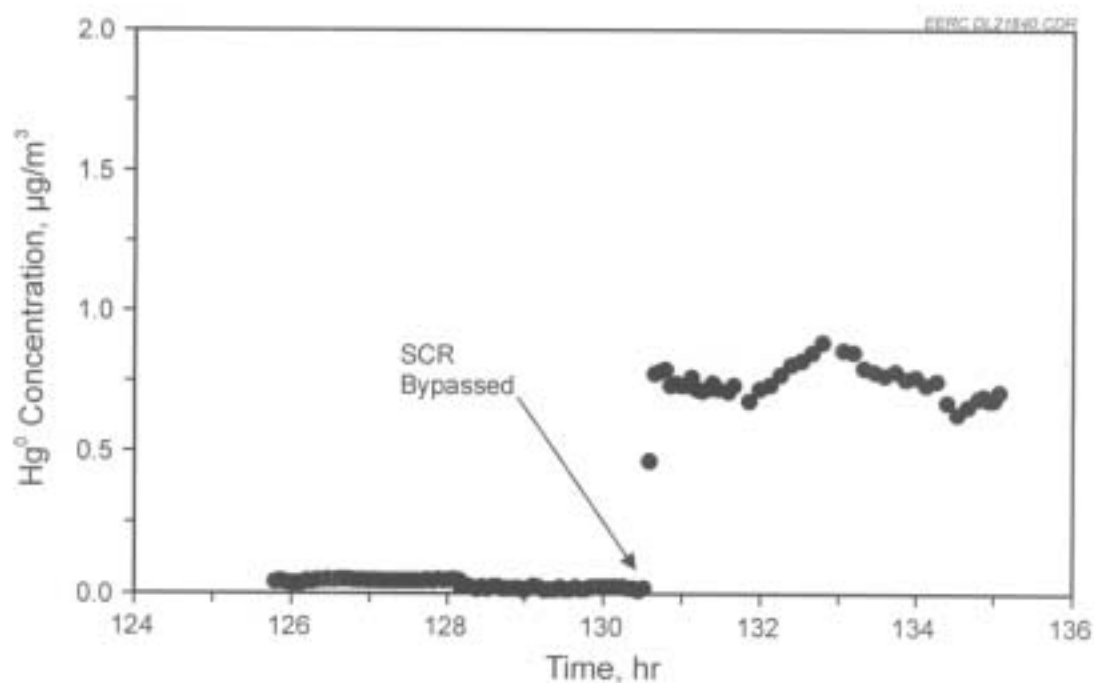
Mercury	Unit	Operation	Average, $\mu\text{g}/\text{m}^3$	Std. Dev., $\mu\text{g}/\text{m}^3$	Upper 90% CI, $\mu\text{g}/\text{m}^3$	Lower 90% CI, $\mu\text{g}/\text{m}^3$
Hg(total)	1	With SCR	5.2	1.7	8.0	2.4
Hg <sup>0</sup>	1	With SCR	0.1	0.2	0.4	0.0
Hg(total)	2	SCR bypassed	5.8	2.7	10.2	1.4
Hg <sup>0</sup>	2	SCR bypassed	0.7	0.5	1.5	0.0
Hg(total)	4	No SCR	7.5	1.0	9.2	5.9
Hg <sup>0</sup>	4	No SCR	1.0	0.4	1.7	0.3



**Figure 5-11**  
**Average Hg<sup>2+</sup> as Measured by Hg SCEMs (total Hg - Hg<sup>0</sup>) for Site S6 Unit 1 (SCR on-line)**



**Figure 5-12**  
Average  $\text{Hg}^{2+}$  as Measured by Hg SCEMs (total Hg -  $\text{Hg}^0$ ) for Site S6 Unit 2 (SCR bypassed)



**Figure 5-13**  
Hg SCEM Results for Site S6 for Unit 2 with SCR Bypassed

### 5.3.4 Coal Analysis Results

Nine of the coal samples from S6 were analyzed for Hg and chlorides (presented in Table B-10 in Appendix B). The Hg concentrations were very consistent, averaging  $0.066 \pm 0.009 \mu\text{g/g}$ . However, the chloride content of the coal was somewhat more variable, averaging  $1020 \pm 300$  ppm. These averages are based on all coal samples analyzed regardless of the unit they were collected from. Plant personnel said that the same coal was fired in all three units.

Additional analyses were conducted on selected coal samples. Results of proximate and ultimate analyses (including the Hg and chloride concentrations for that sample) are provided in Table 5-6. In general, it appears that coal composition from all three units was very consistent.

**Table 5-6**  
**Coal Analysis for Site S6<sup>a</sup>**

Date:		9/24/2002	9/24/2002	10/8/2002	10/8/2002
Unit:		Unit 1 (SCR)	Unit 2 (SCR bypassed)	Composite <sup>b</sup>	Unit 4 (no SCR)
Mercury	ppm (dry)	0.084	0.052	0.063	0.070
Chlorine	ppm (dry)	1210	1520	1170	1320
<i>Proximate Analysis</i>					
Moisture	wt%	5.6	5.9	6.2	6.5
Volatile Matter	wt%	33.1	34.5	34.8	34.7
Fixed Carbon	wt%	49.1	49.1	47.0	47.3
Ash	wt%	12.2	10.5	12.0	11.5
<i>Ultimate Analysis</i>					
Hydrogen	wt%	5.2	5.3	5.3	5.3
Carbon	wt%	70.7	71.0	67.8	68.5
Nitrogen	wt%	1.5	1.7	1.6	1.7
Sulfur	wt%	0.9	0.8	1.2	1.1
Oxygen	wt%	9.5	10.8	12.1	12.0
Heating Value	Btu/lb	11,936	12,142	12,159	11,837
F <sub>d</sub> Factor <sup>c</sup>	dscf/10 <sup>6</sup> Btu	10,357	10,181	9727	10,085

<sup>a</sup> Except where noted, all results are on an as-received basis.

<sup>b</sup> Composite of all three units.

<sup>c</sup> As defined by EPA Method 19.

### 5.3.5 ESP Ash Analysis

ESP hopper ash samples were collected daily throughout the test period from each unit. ESP configuration at Unit 1 (SCR) and Unit 2 (SCR bypassed) consisted of two ESPs in series. Ash samples were obtained from the first hoppers of each ESP (AB and CD) and analyzed for Hg and LOI. Unit 4 (no SCR) had only a single ESP. The ESP hopper ash Hg and LOI averages are presented in Table 5-7. Plant personnel had indicated that ash characteristics were substantially different between the first and second ESP, specifically high unburned carbon in the first ESP.

**Table 5-7**  
**Analysis of ESP Hopper Ash**

Unit	ESP AB				ESP CD			
	Ash Hg, $\mu\text{g/g}$	No. Samples	LOI, %	No. Samples	Ash Hg, $\mu\text{g/g}$	No. Samples	LOI, %	No. Samples
Unit 1 (SCR)	$0.073 \pm 0.014$	22	3.4	4	$0.066 \pm 0.027$	28	3.4	4
Unit 2 (SCR bypassed)	$0.152 \pm 0.068$	20	4.8	5	$0.118 \pm 0.039$	25	4.5	5
Unit 4 (no SCR)	$0.058 \pm 0.017$	14	4.0	2	—	—	—	—

Results from our limited LOI analysis did not indicate a significant difference between the samples.

### 5.3.6 $\text{NH}_3$ Slip and $\text{SO}_3$ Flue Gas Results

$\text{NH}_3$  slip samples were collected at the SCR outlet. A summary of these results is provided in Table 5-8. The  $\text{NH}_3$  slip was less than 0.2 ppm for both samples, indicating an efficiently operating SCR unit. This is also illustrated by >90%  $\text{NO}_x$  removal efficiency calculated from plant operational data.

$\text{SO}_3$  testing was conducted at the SCR outlet and ESP inlet of Unit 1 (SCR) and at the air heater inlet and ESP inlet on Unit 2 (SCR bypassed). A summary of these results is also provided in Table 5-8. These data are consistent with what would be expected from a low-sulfur eastern bituminous coal. It also appeared that (with the exception of the data taken on October 11, 2002) there was some  $\text{SO}_3$  condensation on the fly ash and possibly deposition in the air heater. Comparing the data of Units 1 (SCR) and 2 (SCR bypassed) indicated that there is some conversion of  $\text{SO}_2$  to  $\text{SO}_3$  across the SCR catalyst.



**Table 5-8**  
**Flue Gas SO<sub>2</sub> and NH<sub>3</sub> Results for Site S6<sup>a</sup>**

	SO <sub>2</sub> , ppm		NH <sub>3</sub> Slip, ppm
	SCR Outlet	ESP Inlet	SCR Outlet
<i>Unit 1 (SCR)</i>			
Date	SCR Outlet	ESP Inlet	SCR Outlet
9/23/2002	13.21	4.02	0.11
9/24/2002	14.07	4.19	0.17
<i>Unit 2 (SCR bypassed)</i>			
10/11/2002	5.76	7.68	
10/14/2002	8.17	2.51	

<sup>a</sup> Dry and 3% oxygen.

## 5.4 Mercury Mass Balance

Average Hg concentration in the coal and F<sub>d</sub> factors (Table 5-6) were used to estimate the Hg emission rate at the various sample locations. For the Hg associated with the ESP hopper ash, the F<sub>d</sub> factors were based on the dust-loading measurements as well as the F<sub>d</sub> factor. The results are shown in Table 5-9.

**Table 5-9**  
**Average Mercury Emission Factors for Site S6**

Unit Tested	Coal	lb Hg/10 <sup>12</sup> Btu			%	
		ESP Inlet	ESP Hopper Ash	Stack	Balance <sup>a</sup> Based on Coal Hg	Balance <sup>b</sup> Across ESP
1 (SCR)	5.5	6.1	0.40	7.6	111	131
2 (SCR bypassed)	5.5	7.3	0.93	5.5	87	88
3 (no SCR)	5.5	—	0.31 <sup>c</sup>	4.5	—	—

<sup>a</sup> Calculated balance is based on the coal Hg concentration and the ESP inlet  $[(\text{Hg}_{\text{coal}} - \text{Hg}_{\text{ESP inlet}})/\text{Hg}_{\text{coal}}]$ .

<sup>b</sup> Calculated balance is based on the ESP inlet Hg concentration and the stack  $[(\text{Hg}_{\text{stack}} + \text{Hg}_{\text{ESP hopper}})/\text{Hg}_{\text{ESP inlet}}]$ .

<sup>c</sup> The ESP inlet was not measured; therefore, the inlet dust loading used was that obtained from Unit 2 (SCR bypassed).

As shown in Table 5-9, it appears that the Hg concentration as measured in the coal is low compared to the flue gas measurements. The variability of the coal Hg was very low with a relative standard deviation of <15%. The variability of the flue gas data also was low. The relative standard deviations ranged from 11% to 22%.

## 5.5 General Observations from S6

- There was Hg oxidation across the SCR catalyst as the percentage of  $\text{Hg}^{2+}$  in the flue gas increased from 60% to 82%. At the ESP inlet and outlet location, the percentage was 87%.
- Comparing the Hg speciation results (at the ESP inlet location) with and without SCR in service showed that the presence of SCR resulted in greater  $\text{Hg}^{2+}$ : 69% for Unit 2 (SCR bypassed) and 87% for Unit 1 (SCR).
- Hg SCCEM data gathered during the time SCR was bypassed illustrate a small but measurable increase in  $\text{Hg}^0$  from approximately 0.1 to 0.75  $\mu\text{g}/\text{m}^3$ .
- There was little if any Hg removal across the ESP.



# 6

## DISCUSSION OF OVERALL RESULTS

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The primary goal of this program has been to evaluate the effect of SCR operation on Hg speciation with a focus on quantifying the fate of Hg across various pollution control devices. Over the course of 2 years, a total of six plants have been tested with two of these plants being tested in both 2001 and 2002, providing a total of eight data sets from which to evaluate the effects of SCR operation. A summary of the plant configurations and the type of coal combusted is provided in Table 6-1. A summary of the coal fired at each facility is shown in Table 6-2.

It should be noted that additional data had been generated in 2001 for facilities that utilized either SNCR or flue gas conditioning technologies; however, for the purposes of this report, only SCR facilities are being addressed. Results from SNCR and flue gas conditioning plants can be found in the *Power Plant Evaluation of the Effect of Selective Catalytic Reduction in Mercury* [11].

As has been stated earlier, the use of SCR to reduce NO<sub>x</sub> emissions has the potential to improve the Hg control efficiency of existing particulate removal and FGD systems by promoting Hg<sup>2+</sup> or particulate-bound Hg formation. As data were compiled at the various facilities, several factors were identified which may potentially impact the oxidation potential of SCR. Among these factors, coal type, catalyst type and structure, and catalyst age were specifically identified as factors that have the potential to influence Hg speciation.

To evaluate the effect of SCR on Hg speciation and, ultimately, on Hg emission at each plant, the following were determined:

- The change in Hg oxidation across the SCR unit.
- The effect of SCR on Hg oxidation obtained by comparing results with and without SCR in service at the particulate control inlet or outlet.
- The overall Hg removal with and without SCR.

**Table 6-1**  
Summary of SCR Program Plant Configuration

Plant	Coal	Boiler Type	Boiler Size, MW	Low-NO <sub>x</sub> Burners	Catalyst Vendor and Type	Catalyst Age	SCR Space Velocity, hr <sup>-1</sup>	Particulate Control	Sulfur Control
S1 <sup>a</sup>	PRB subbit.	Cyclone	650	No	Cormetech honeycomb	2 ozone seasons	1800	ESP	None
S2	OH bit.	Wall-fired	1360	Yes	Siemens/Westinghouse plate	3 months	2125	ESP	Wet FGD <sup>b</sup>
S3	PA bit.	Tangential-fired	750	Yes, with overfire air	KWH honeycomb	1 ozone season	3930	ESP	None
S4	KY bit.	Cyclone	704	No	Cormetech honeycomb	1 ozone season	2275	Venturi scrubber	Venturi scrubber <sup>c</sup>
S5	WV bit.	Wall-fired	684	Yes	Halder-Topsoe plate	3 months	3700	ESP	Wet FGD <sup>b</sup>
S6	Low-sulfur KY and WV bit.	Concentric-fired	700	Yes	Cormetech honeycomb	2 ozone seasons <sup>d</sup>	3800	ESP	None
S2-2 <sup>e</sup>	OH bit.	Wall-fired	1350	Yes	Siemens/Westinghouse plate	2 ozone seasons	2125	ESP	Wet FGD <sup>b</sup>
S4-2 <sup>e</sup>	KY bit.	Cyclone	650	No	Cormetech honeycomb	2 ozone seasons	2275	Venturi scrubber	Venturi scrubber

<sup>a</sup> Not discussed in detail in this report.

<sup>b</sup> Magnesium-enhanced lime FGD.

<sup>c</sup> Combined particulate and SO<sub>2</sub> limestone venturi scrubber.

<sup>d</sup> One layer of catalyst was replaced after one ozone season.

<sup>e</sup> Plant was restarted in 2002.

**Table 6-2**  
**Average Analysis of Coals Fired During 2001 and 2002 Field Tests<sup>a</sup>**

	S1	S2	S2-2	S3	S4	S4-2	S5	S6
Hg, $\mu\text{g/g}$ dry	0.10	0.17	0.14	0.40	0.13	0.16	0.13	0.073
Cl, $\mu\text{g/g}$ dry	<60	1330	635	1150	360	260	470	1020
Moisture, %	27.5	7.6	6.1	7.0	10.5	11.8	4.6	6.1
Ash, %	3.7	11.7	9.4	14.0	9.1	8.5	12.1	11.6
Sulfur, %	0.2	3.9	3.9	1.7	2.9	2.8	3.6	1.0
HV, Btu/lb	8977	11,092	12,097	11,421	11,341	11,634	12,120	12,019

<sup>a</sup> As-received unless otherwise noted.

## 6.1 The Change in Mercury Oxidation Across the SCR Catalysts

The percentage of  $\text{Hg}^{2+}$  was measured at both the inlet and outlet of the SCR unit at each facility. It should be noted that all of the OH samples taken at these two locations were prior to the air preheater; therefore, the temperature ranged from 640° to 700°F (338°–371°C). Table 6-3 presents the results of the 2001 and 2002 testing. For all of the plants tested, there was an increase in Hg oxidation across the SCR catalyst. However, the amount of oxidation that occurs across the catalyst is highly variable. Some factors that may affect the level of oxidation are coal, catalyst chemistry and structure, and catalyst age.

There was substantial variability in the percentage of  $\text{Hg}^{2+}$  at both the SCR inlet and outlet locations. Site S1 fired a PRB coal and had a very high level of LOI, and as such, it is not surprising it would be different, but there was also variability among the other sites firing eastern bituminous coal. For example, repeat testing conducted at Site S4 indicated a substantial increase in the percentage of  $\text{Hg}^{2+}$  when the coal chloride concentration increased from 2001 to 2002 testing. As shown in Figure 6-1, one factor that appears to relate to the percentage of  $\text{Hg}^{2+}$  at the inlet to SCR unit is the chloride concentration in the coal. It appears there is a threshold chloride concentration at about 300 and 500 ppm chloride above which 40%–60% Hg oxidation results at the SCR inlet. What effect this has on overall Hg oxidation is unclear.

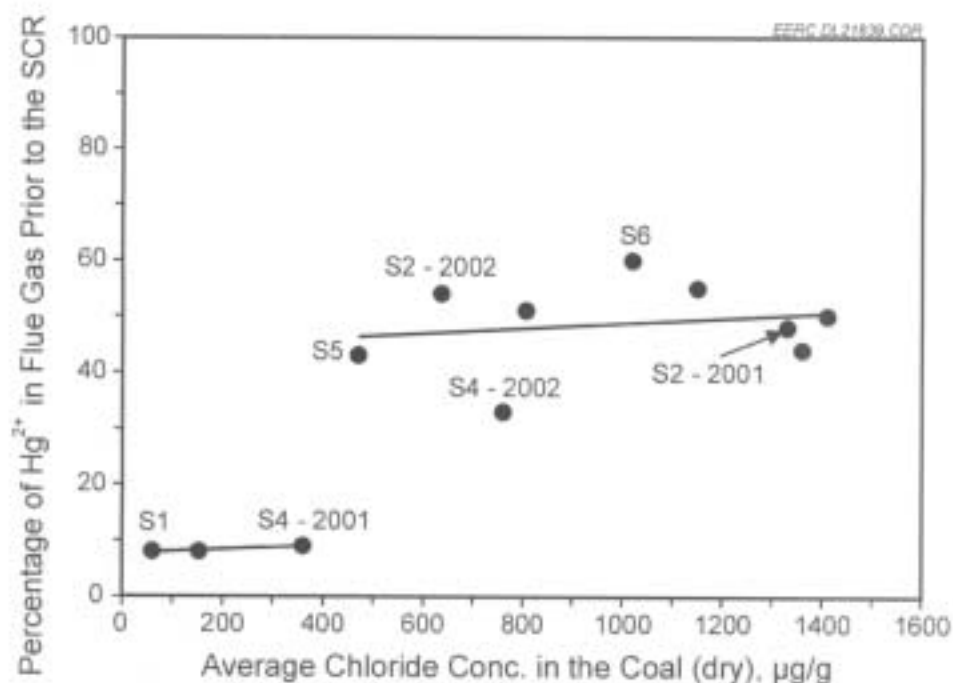
Once the flue gas enters the SCR unit, it would be expected that other factors such as catalyst type, structure, and space velocity may impact Hg oxidation. Without substantially more data, it is very difficult to determine the effects of these parameters. For example, Sites S2 and S4 had “low” space velocities (<2300  $\text{hr}^{-1}$ ); Sites S3, S5, and S6 had “high” space velocities (>3700  $\text{hr}^{-1}$ ), but there does not appear to be a clear correlation. However, as shown in Table 6-1, the catalyst types and structures were also different. An attempt was made to evaluate catalyst aging effects by retesting two plants in 2002 that had been sampled in 2001: Sites S2 and S4. The results are discussed in Section 6.3. EPRI is currently in the process of trying to develop models that would predict the effects of the SCR catalysts based on catalyst properties.

**Table 6-3**  
Change in Mercury Oxidation Across the SCR Catalyst

Site	Year Sampled	SCR Inlet Hg <sup>2+</sup> , % of total Hg	SCR Outlet Hg <sup>2+</sup> , % of total Hg	Percentage Point Increase, <sup>a</sup> %
S1 <sup>b</sup>	2001	8	18	10
S2	2001	48	91	43
S2	2002	54	87	33
S3	2001	55	65	10
S4	2001	9	80	71
S4	2002	33	63	30
S5	2002	43	76	33
S6	2002	60	82	22

<sup>a</sup> Percentage point increase is defined as (SCR Outlet % - SCR Inlet %).

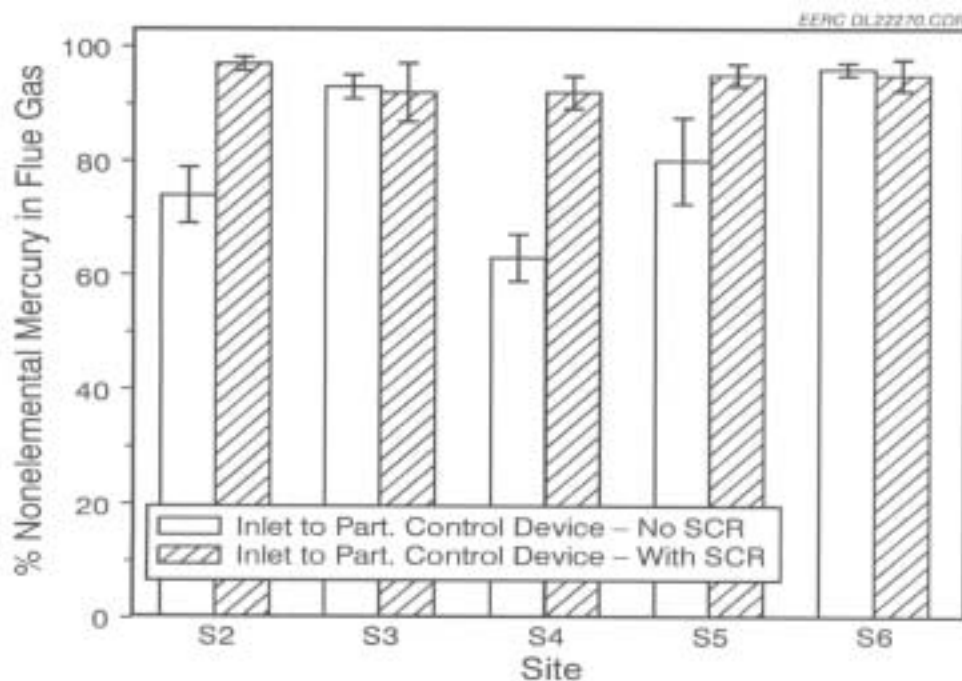
<sup>b</sup> Site S1 fired a PRB coal; the others were eastern bituminous coals.



**Figure 6-1**  
Percent of Oxidized Hg<sup>2+</sup> at the Inlet of the SCR System as a Function of Chloride Content of the Coal (note: nonlabeled data points are results from plants without SCR units where Hg speciation was measured at the air heater inlet)

## 6.2 Effect of the SCR on Mercury Oxidation

Although there is strong evidence that an SCR catalyst does promote Hg oxidation, to determine the overall effect of SCR, it was useful to conduct tests both with and without SCR in service at each site. For two of the sites (S3 and S4), testing was done on the same unit with SCR bypassed at the end of the ozone season. For one, S5, sampling was done at two similar units with only one having an SCR unit. At the final site, S6, two units were tested, and both had SCR units, but the SCR unit on one was bypassed. Figure 6-2 shows the comparison for all of the sites firing eastern bituminous coal. Based on Figure 6-2, it appears (with the possible exception of Site S3) there is increased Hg oxidation as a result of SCR based on measurements made at the inlet to the particulate control device. Table 6-4 quantifies the change in  $\text{Hg}^{2+}$ .



**Figure 6-2**  
Mercury Speciation Results Comparing All the Sites Tested Firing Eastern Bituminous Coal



**Table 6-4**  
**Net Change in Hg<sup>2+</sup> as Measured at the Inlet to the Particulate Control Device**

Site	With SCR, %	Without SCR, %	Percentage Point Increase, %
S2-01	97	73	24
S2-02	97	— <sup>a</sup>	—
S3	67	77	-10 <sup>b</sup>
S4-01	87	56	31
S4-02	96	57	39
S5	95	80	15
S6	87	69	18

<sup>a</sup> OH samples were not taken in 2002; however, based on Hg SCEM data, it did not appear the change was as great in 2002 as 2001. The Hg SCEM result showed the Hg<sup>0</sup> concentration only increasing from 0 to 0.8 µg/m<sup>3</sup> at the ESP inlet locations (with and without the SCR in service). In 2001, the Hg<sup>0</sup> increased from 0.4 to 3.4 µg/m<sup>3</sup> when the SCR was bypassed.

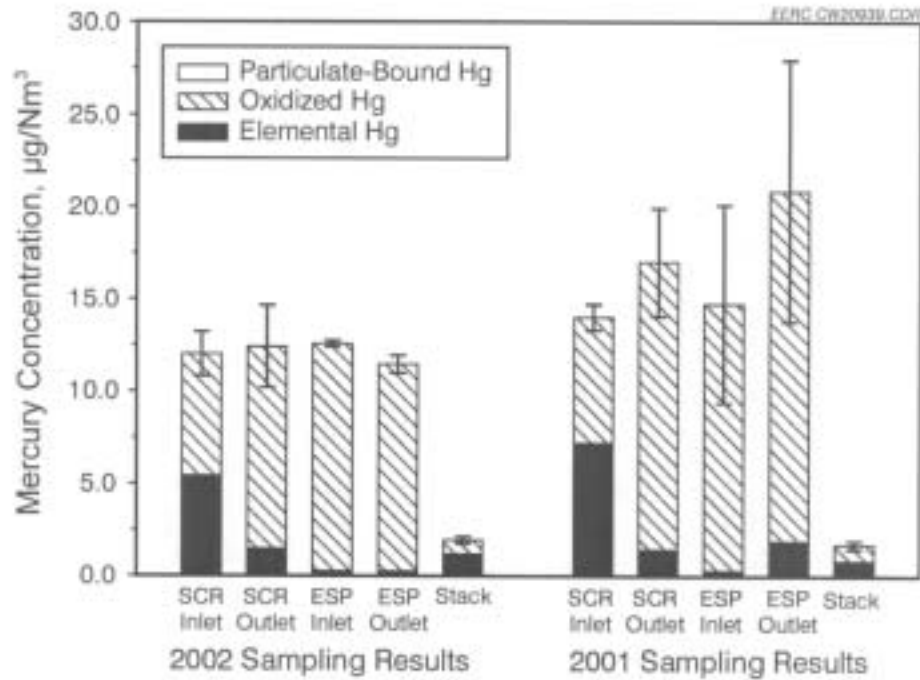
<sup>b</sup> If the particulate-bound Hg is included, the results are 81% nonelemental Hg both with and without the SCR.

### 6.3 Effect of SCR Catalyst Age on Mercury Speciation

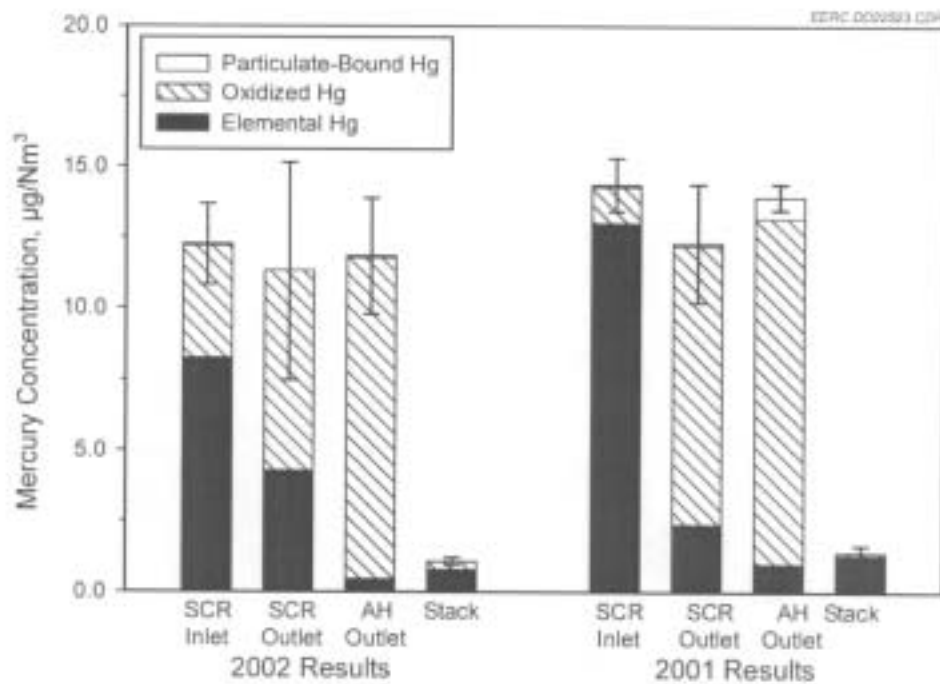
Flue gas monitoring was conducted over 2 consecutive years at two power plants to evaluate the impact catalyst age had on Hg speciation. Sites S2 and S4 were tested in 2001 and again in 2002 to determine if the oxidation potential of an SCR catalyst was reduced with time, specifically after one additional season of operation.

Testing in 2001 at Site S2 was conducted after approximately 3.5 months of catalyst age and about 5 months at Site S4. 2002 testing was conducted after an additional ozone season, approximately 5 months of catalyst age. Figures 6-3 and 6-4 show there was a decrease in Hg oxidation across the SCR catalyst in 2002 compared to 2001 for both sites retested. However, there were mitigating circumstances at each plant. At Site S2, in an attempt to control SO<sub>3</sub> emissions, humidification and alkali injection were done upstream of the SCR unit. As a result of humidification, the temperature of the SCR unit was cooler by about 10°F in 2002 compared to 2001. In addition, the coal fired at S2 was from a different mine than that used in 2001. At Site S4, the coal chloride concentration was extremely variable in 2001.

Although there were differences in the oxidation across the SCR catalyst, at the inlet to the particulate control device there was no significant difference between the 2 years for either Site S2 or S4. Although there are suggestions that Hg oxidation may have decreased after an additional ozone season, the results are considered to be inconclusive. Additional testing is being planned. Hg speciation sampling is recommended at these two plants for several more years.



**Figure 6-3**  
Comparison of Mercury Speciation Results from 2001 and 2002 at Site S2



**Figure 6-4**  
Comparison of Mercury Speciation Results from 2001 and 2002 at Site S4

## 6.4 SCR/Wet FGD Combination for Mercury Control

The underlying intent of understanding Hg oxidation via SCR technology is to determine its potential to improve the Hg collection efficiency of existing ESPs, fabric filters and, in particular, FGD systems. In general, wet FGD systems remove a large percentage (>90%) of  $\text{Hg}^{2+}$ . However, there has been evidence that some of the captured  $\text{Hg}^{2+}$  can be reduced in the wet FGD system to  $\text{Hg}^0$  [11,19]. Three sites have been tested in 2001 and 2002 that have wet FGD systems. Sites S2 and S5 employ magnesium-enhanced lime FGDs, and Site S4 is a combined particulate/ $\text{SO}_2$  venturi/spray tower scrubber. Sites S2 and S4 were tested in 2001 and 2002, thus yielding a database of five measurements at three sites. It is important to note that ~60% of wet FGD systems in the United States are limestone forced-oxidation systems. As can be seen in Table 6-5, at all of the sampling sites when SCR was not in service, there is a measurable increase in  $\text{Hg}^0$  across the FGD unit. For the tests with SCR in service, the five data points show an increase in  $\text{Hg}^0$ , but the increase appears to be very small and is generally within the variability of the data.

**Table 6-5**  
**Effect of the SCR on  $\text{Hg}^0$  Concentration Across the Wet FGDs**

Site	Year Sampled	FGD Inlet $\text{Hg}^0$ Conc., $\mu\text{g}/\text{Nm}^3$	FGD Outlet $\text{Hg}^0$ Conc., $\mu\text{g}/\text{Nm}^3$	Change, <sup>a</sup> $\mu\text{g}/\text{Nm}^3$	Total Hg Removed, %
<b>With SCR</b>					
S2	2001	0.4 <sup>b</sup>	0.9	0.5	89
S2	2002	0.3	1.3	1.0	84
S4	2001	0.5	0.8	0.3	90
S4	2002	1.0	1.3	0.3	91
S5	2002	0.7	1.0	0.3	91
<b>Without SCR</b>					
S2	2001	3.4 <sup>b</sup>	5.0	1.6	51
S4	2001	5.6	7.1	1.5	46
S4	2002	5.7	8.0	2.3	44
S5	2002	4.7	6.1	1.4	51

<sup>a</sup> Change is defined as: (FGD outlet  $\text{Hg}^0$  conc. - FGD inlet  $\text{Hg}^0$  conc.).

<sup>b</sup> For 2001 Site S2 data, the ESP inlet data were used because the FGD inlet Hg concentrations were clear outliers.

The mechanism for FGD reemission is not well understood, but it is speculated that sulfite in the FGD slurry may reduce  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ . The impact of forced oxidation may alter the sulfite chemistry, potentially giving different results than those obtained for the plants shown in Table 6-5. Because the mechanism of reemission is not well understood and it is not known how

SCR units may impact reemission, the reader is cautioned in attempting to extrapolate the results from these three sites to all FGD systems. Additional studies are recommended and planned at plants with limestone forced-oxidation FGD systems.



# 7

## CONCLUSIONS

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The primary conclusions based on the test results are:

- For plants firing eastern bituminous coals, Hg oxidation occurs across SCR catalysts. However, it appears to be variable and most likely related to a variety of factors. Some potential factors are coal characteristics, catalyst chemistry, catalyst type and structure, space velocity, and catalyst age.
- It appears that addition of an SCR unit, when an eastern bituminous coal is fired, will provide additional  $\text{Hg}^{2+}$ . With the exception of Site S3 (where the Hg was essentially all  $\text{H}_2^{2+}$  or  $\text{Hg}_0$ , both with and without SCR), all facilities showed increased oxidation at the inlet to the particulate control device. The increase ranged from 15 to 39 percentage points.
- At both sites where sampling was done in 2001 and 2002, there appeared to be a decrease in Hg oxidation across the SCR catalyst between one and two ozone seasons of operation. However, at both facilities, there were other possible explanations related to changes in plant operation. These changes do not allow a definitive conclusion to be developed on the effect of an additional ozone season on SCR/Hg oxidation. It is important to note that the Hg oxidation at the inlet to the particulate control device was not affected by the additional ozone season.
- Based on the limited data at three plants (five total data sets), it appears there is some reemission of the captured Hg across the wet FGDs. For the tests with SCR in service, the increase appears to be very small and is generally within the variability of the data. Nevertheless, five data points show an increase in  $\text{Hg}^0$ . When an SCR unit is not present, it appears that the reemission is more pronounced.

### Future Test Plans

Based on a review of these test results, several areas are recommended for further investigation. DOE, EPA, and EPRI are planning to conduct additional full-scale, as well as bench- and pilot-scale studies, to address the following:

- The effect of SCR when PRB coal is fired in a pc-fired boiler
- Further testing to determine the effect of SCR units on Hg capture in wet FGD systems, in particular on Hg reemission
- The effect of SCR when PRB/bituminous-blended coal is fired
- Further evaluation of the effect of catalyst age on Hg speciation



# 8

## QUALITY ASSURANCE/QUALITY CONTROL

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The EERC is committed to delivering consistent and high-quality research that exceeds its clients' needs and expectations. To ensure that the goals of this project are realized, an organizationwide quality management system (QMS), authorized and supported by EERC managers, is in effect and governs all programs within the organization. The EERC established and formalized a QMS and QC procedures in August 1988. The Quality Manual defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program. Compliance with this manual and its supporting documents ensures that the EERC adequately fulfills governmental and private client requirements relating to quality and compliance with applicable regulations, codes, and protocols. This project was required to follow the Quality Manual, project-specific quality assurance (QA) procedures, and all revisions. The EERC Quality Assurance Manager implements and oversees all aspects of QA/QC for all research, development, and demonstration projects and reviewed the QA/QC components of this project. The project manager is responsible for ensuring that project-specific QA/QC protocols are followed.

To ascertain data quality obtained during the sampling program, the following procedures were used:

- Process operating data were examined to ensure that the OH sampling took place during steady, representative plant operation.
- Sampling and analytical analysis protocols were reviewed to ascertain how the data compared with other data generated using standard protocols.
- The reagent blanks, field blanks, and field spikes were reviewed to qualitatively determine the confidence that can be placed in the results.
- The QA/QC data results were then compared with data quality indicators to qualitatively determine the validity of the data in terms of variability and accuracy.

### 8.1 Process Data Evaluation

Plant operating data were examined to ensure that process operation was stable and representative during the OH sampling periods. Excessive scatter or significant trends in relevant process variables can indicate periods of unrepresentative unit operation. Data scatter is useful for identifying periods of operational difficulty; data trends indicate periods when steady-state operation has not been achieved. It was the intent for the Hg SCEMs to be operated both during steady-state conditions and during any upset conditions that occurred. Plant data, to the extent



available, were plotted for each of the test sites. In general, it appears that all of the OH sampling occurred either when the unit was at or near full-load conditions. When plant operational upsets occurred during OH sampling, sampling was suspended, and a new sample was taken after the plant was operating at more normal conditions. This occurred at Site S5 and is illustrated by the greater quantity of OH results.

## **8.2 Sampling Quality Control Evaluation**

Sampling precision can be estimated by comparing the results of various parameters of replicate samples, notably, velocity, moisture content, and gas composition in the stack. Sampling accuracy is usually inferred from the calibration and proper operation of the equipment and from historical validation of the methods. Field blanks are used to determine any biases that may be caused by contamination or operator errors. A field blank is defined as a complete impinger train, including all glassware and solutions, which is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps are taken to eliminate or reduce the contamination to below background levels. The results of the blanks can be seen in Appendix B (Tables B-1, B-3, B-5). In almost all cases, the field blank results were less than detection limits. For the few samples where a detectable level of Hg was measured, the concentration was low enough to be insignificant compared to the measured flue gas concentration for that Hg species.

Sampling comparability depends on whether the samples are representative and on the use of standard methods consistently applied. All methods used for the project were standard American Society for Testing and Materials or EPA sampling methods. Sampling completeness is primarily a function of providing the requisite number of samples to the analytical laboratory. In most cases, this consisted of duplicate samples.

The isokinetic sampling rate is a measure of the operational performance of sampling for particulate matter. The normal acceptance criterion for isokinetic variation is 10%. With over 90 OH samples taken during this project, five samples were outside the  $\pm 10\%$  range. Four samples were collected at the stack and, based on the very low particulate loading and Hg concentration, appeared to have no significant impact on the results. One sample, collected at the ESP outlet location, had an isokinetic measurement of greater than 100%. Again, the Hg results from this sample were not significantly affected because of the extremely low concentration of Hg and low particulate loading. A lower-than-expected isokinetic sampling rate results in an overestimation of the larger particles, resulting in an inflated dust-loading estimate. However, for these samples, the dust loading and the Hg concentrations were very similar to the other samples taken. It is believed that this deviation from the accepted isokinetic value had no significant impact on the overall conclusions.

One known concern with the OH method is a bias that occurs as a result of the close contact between the flue gas and the fly ash collected on the sampling filter. This is particularly true at high-dust sampling locations such as SCR inlet, outlet, and the inlet to the particulate control device. The degree of bias is dependent on the reactivity of the ash collected on the filter and the

flue gas temperature. This ash has the potential to adsorb or oxidize Hg. The only method of determining the extent to which the bias occurs is to compare the inlet and outlet ESP Hg<sup>0</sup> results. If there is an increase in Hg<sup>0</sup> concentration across the ESP, it indicates some oxidation occurred across the sampling filter. To determine if there was adsorption of Hg on the sample, resulting in a high particulate-bound Hg bias, the filter concentration is compared to the ESP hopper ash samples. Although representative ash samples are extremely difficult to collect from an ESP, it is possible to obtain an indication as to whether the filter is biasing the particulate-bound Hg concentration. These comparisons were made, and the results from each facility are detailed in the discussion in Sections 2–7.

### 8.3 Evaluation of Measurement Data Quality

An evaluation of the measurement data quality is based on QC data obtained during sampling and analysis. Generally, the type of QC information obtained pertains to measurement precision, accuracy, and blank effects, determined by collecting various types of replicate, spiked, and blank samples. The specific characteristics evaluated depend on the type of QC checks performed. For example, if problems with contamination occur, blank samples can be prepared at different stages in the sampling and analysis process to isolate the source of a blank effect. Similarly, replicate samples may be generated at different stages to isolate and measure the sources of variability. Table 8-1 summarizes the QA/QC measures used and the characteristic information obtained for this project.

As shown in Table 8-1, different QC checks provide different types of information, particularly pertaining to the sources of inaccuracy, imprecision, and blank effects. In general, measurement precision and accuracy are typically estimated from QC indicators that cover as much of the total sampling and analytical process as feasible. Precision and accuracy estimates are based primarily on the actual sample media documenting the precision and accuracy actually obtained, and the objectives serve as benchmarks for comparison. The effects of not meeting the objectives need to be considered in light of the intended use of the data. The results of the field and media spikes that were done as part of this project are shown in Appendix B (Tables B-2, B-4 and B-6). As can be seen in these tables, the spike recovery was excellent for field blanks completed. Although blank filters are routinely analyzed for Hg to ensure no Hg contamination on the sample, no field filter spikes were completed for the project. However, in the laboratory, known Hg calibration standards are routinely analyzed.

Other specific QC procedures that were used to measure Hg in the flue gas for this project are as follows:

- **Instrument Setup and Calibration.** The instrument used in the field for Hg determination was a Leeman Labs PS200 cold-vapor atomic absorption spectrometer. To measure Hg, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% w/v stannous chloride in 10% v/v HCl as the reductant. Each day, the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% v/v HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for the

**Table 8-1**  
**Elements of the QA/QC Plan**

QC Activity	Characteristic Measured
<b>Precision</b>	
Replicate Samples Collected over Time under the Same Conditions	Total variability, including process or temporal, sampling, and analytical but not bias.
Duplicate Field Samples Collected Simultaneously	Sampling plus analytical variability at the actual sample concentrations.
Duplicate Analyses of a Single Sample	Analytical variability at the actual sample concentrations.
Media-Spiked Duplicates	Sampling plus analytical variability at an established concentration.
Laboratory Control Sample Duplicates	Analytical variability in the absence of sample matrix effects.
<b>Accuracy (including precision and bias)</b>	
Media-Spiked Samples	Analyte recovery in the sample media, indicating possible interferences and other effects. In a single sample, includes both random error (imprecision) and systematic error (bias).
Laboratory Control Samples	Analyte recovery in the absence of actual sample matrix effects. Used as an indicator of analytical control.
<b>Blank Effects</b>	
Field Blank	Total sampling plus analytical blank effect, including sampling equipment and reagents, sample transport and storage, and analytical reagents and equipment.
Reagent Blank	Blank effects from reagents used.

given standard was then logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized to verify the calibration. This QC standard is prepared from a different stock than the calibration standards. It was required that the values obtained read within 5% of the true value before the instrument was used. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument. The results of these calibrations are available upon request of any EERC client.

- **Presampling Preparation.** All data sheets, volumetric flasks, and Petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The outlet filter samples were placed in premarked Petri dishes and taken back to the EERC, where they were

analyzed using mixed-acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

- **Glassware and Plasticware Cleaning and Storage.** All glass volumetric flasks and transfer pipettes used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10%  $\text{v/v}$  nitric acid for a minimum of 4 hr, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant. All glassware cleaning solutions are periodically checked for Hg. In all cases, the measured Hg concentration was below detection limits.
- **Analytical Reagents.** All acids to be used for the analysis of Hg were trace metal-grade or analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within 0.5% and were traceable to National Institute of Standards and Technology standard reference materials.

## 8.4 OH Method Error Analysis

The precision of Hg measurements is estimated to be in the order of  $\pm 10\%$ – $30\%$ , depending upon the total Hg concentration, its proximity to the method detection limit and, possibly, other flue gas constituents. In addition, flue gas sampling at internal streams such as the SCR inlet and outlet and the ESP inlet are often single-point samples, may not be uniform (stratified), and thus may not represent the true flue gas distribution of the power plant. These uncertainties in the total Hg measurements must be taken into account when data are interpreted. However, these uncertainties are not expected to have a significant effect on the overall conclusions of this study.

For example, if the “actual” Hg concentrations at the ESP inlet and the stack are 10 and 1 lb/trillion Btu, respectively, then the total Hg removal would be 90%. If the measurements at both the inlet and outlet were assumed to have a  $\pm 20\%$  error, then the inlet concentration could be measured at either 8 or 12 lb/trillion Btu and the outlet concentration at either 1.2 or 0.8 lb/trillion Btu. The estimated Hg removal could range from as low as 85% to as high as 93%.

The calculated Hg removal is much more sensitive at sites where the Hg removal efficiencies are very low. For example, if the “actual” Hg concentrations at the ESP inlet and the stack were 10 and 9 lb/trillion Btu, respectively, then the total Hg removal would be 10%. If the measurements at both the inlet and outlet were assumed to have a  $\pm 20\%$  error, then the inlet concentration could be measured at either 8 or 12 lb/trillion Btu and the outlet concentration at either 7.2 or 11.8 lb/trillion Btu. Thus the calculated Hg removal could range from as low as  $-48\%$  to as high as 40%.



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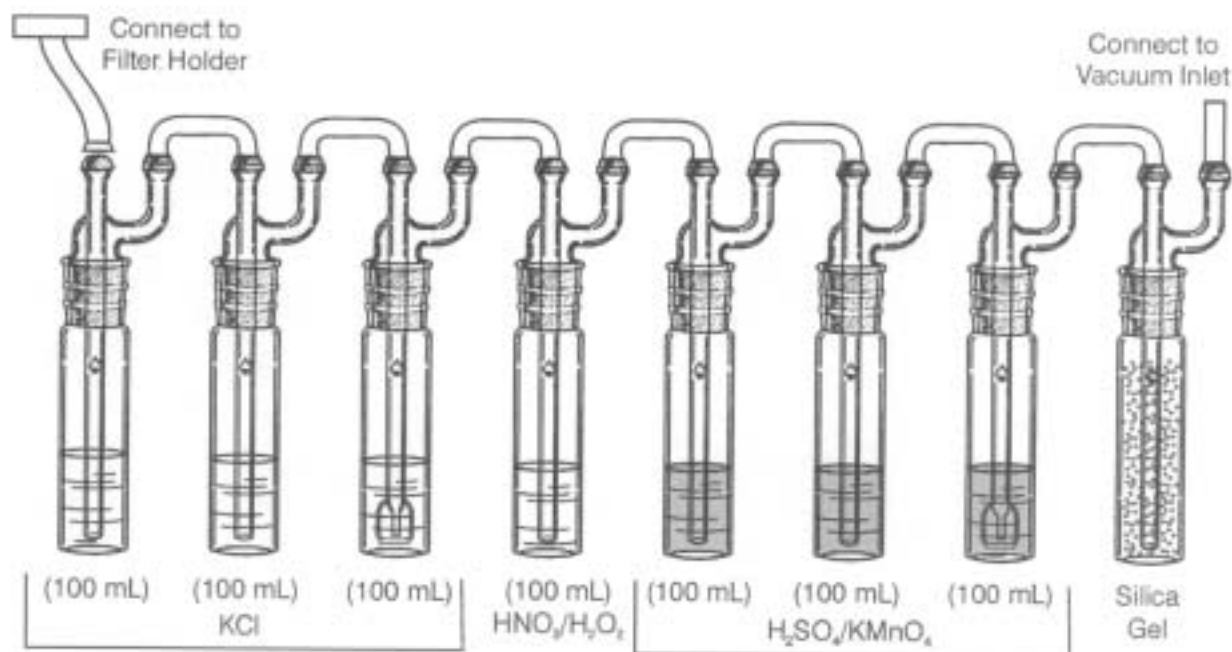
## SAMPLING METHODS AND PROCEDURES

This appendix provides the template for developing site-specific test plans and sampling protocols.

### Ontario Hydro Mercury Speciation Method (OH method)

This is a summary of the sampling and analytical procedures used to conduct the mercury (Hg) speciation method entitled "Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)." The American Society for Testing and Materials D22 committee has accepted the method, and the exact method details are provided on the U.S. Environmental Protection Agency (EPA) Web page at <http://www.epa.gov/ttn/emc/prelim.html> under Preliminary Method 3. All other EPA methods are also found at the same emission measurement Web address.

The OH method follows standard EPA methods for isokinetic flue gas sampling (EPA Methods 1–3 and EPA Method 5/17). Figure A-1 presents a schematic of the Hg speciation sample train.



EEHC K013181.COH

**Figure A-1**  
**Schematic of the OH Mercury Speciation Train**



Table A-1 presents a list of sample train components for the OH configuration.

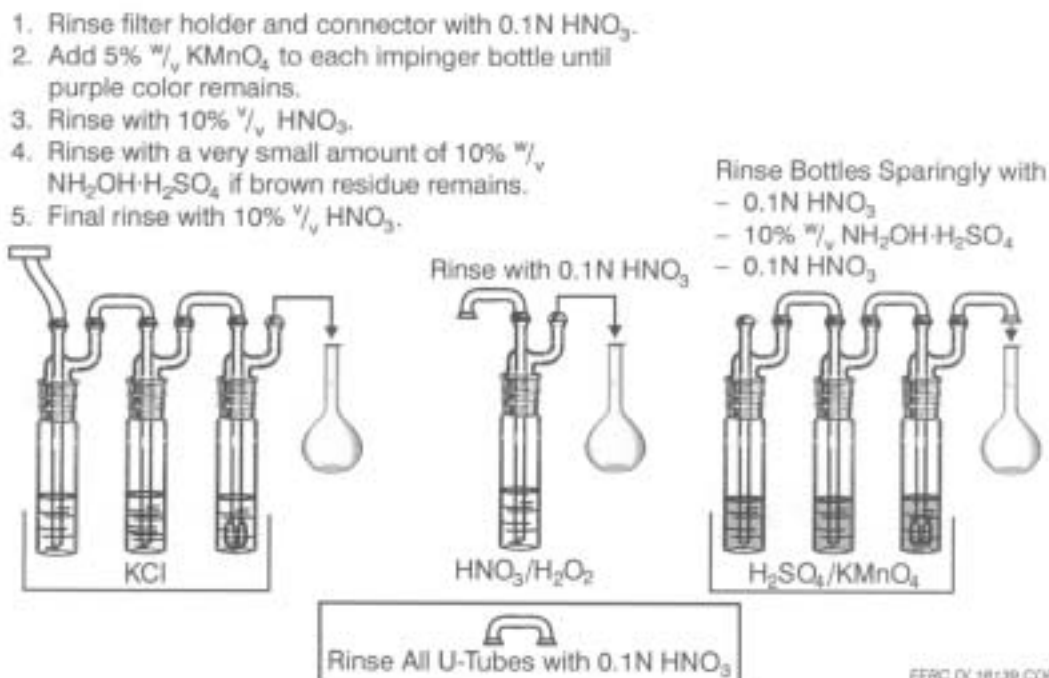
**Table A-1**  
**Sample Train Components for the OH Method**

Component	Details
Nozzle	Glass, quartz, or Teflon-coated stainless steel
Filter	Quartz, in glass or Teflon-coated stainless steel holder
Probe	Glass or Teflon, heated to gas temperature
Connector Line	If needed, Teflon line used to connect from probe to impingers, heated to a minimum of 248°F (120°C).
Impingers 1 and 2	1 mol/L KCl solution; modified Smith Greenburg (SG) impinger
Impinger 3	1 mol/L KCl solution; standard SG impinger
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger
Impingers 5 and 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger
Impinger 8	Silica gel; modified SG impinger

A sample is withdrawn from the flue gas stream isokinetically through the filtration system, which is followed by a series of impingers in an ice bath. Particulate-bound Hg is collected on the front half and filter;  $\text{Hg}^{2+}$  is collected in impingers containing 1 N potassium chloride solution; and elemental Hg is collected in one impinger containing a 5% nitric acid and 10% peroxide solution and three impingers containing a solution of 10% sulfuric acid and 4% potassium permanganate. An impinger containing silica gel collects any remaining moisture. The filter media is quartz fiber filters. The filter holder is glass or Teflon-coated. An approximate 2-hr sampling time was used, with a target sample volume of 1–2.5 standard cubic meters.

Figure A-2 is a schematic of the sample recovery procedure for the impinger train. The samples were recovered into precleaned glass bottles with vented Teflon-lined lids. The following sample fractions were recovered (specific rinse solutions are contained in the method):

1. The sample filter
2. The front-half rinse (includes all surfaces upstream of the filter)
3. Impingers 1 through 3 (KCl impingers) and rinses
4. Impinger 4 ( $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) and rinses
5. Impingers 5–7 ( $\text{H}_2\text{SO}_4/\text{KMnO}_4$  impingers) and rinses



**Figure A-2**  
**Sample Recovery Scheme for the OH Mercury Speciation Train**

- Impinger 8 (silica gel impinger [note that this sample is weighed for moisture determination and not included in the Hg analysis])

The sample fractions were prepared and analyzed as specified in the method and summarized below:

- Ash Sample (Containers 1 and 2)** – The particulate catch was analyzed using EPA Method 7043 or equivalent (see Table 3) or using a Milestone DMA-80 Hg analyzer. However, if the particulate catch was less than 1 gram (as was the case at the outlet of the particulate control device), the entire sample of the particulate collected on the filter (including the filter) was subsequently digested using EPA Method 3051, followed by analysis using EPA 7471A.
- KCl Impingers (Container 3)** – The impingers were prepared using  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{KMnO}_4$  solutions as specified in the method.
- $\text{HNO}_3/\text{H}_2\text{O}_2$  (Container 4)** – The impinger solutions were prepared using  $\text{HCl}$  and  $\text{KMnO}_4$  solutions as specified in the method.
- $\text{H}_2\text{SO}_4/\text{KMnO}_4$  Impingers (Container 5)** – The impinger solutions were prepared using hydroxylamine hydrochloride as specified in the method.

Each prepared fraction was analyzed for total Hg by cold-vapor atomic absorption (CVAA). CVAA is a method based on the absorption of radiation at 253.7 nm by Hg vapor. The Hg is reduced to the elemental state and aerated from solution in a closed system. The Hg vapor passes through a cell positioned in the light path of an atomic absorption (AA) spectrometer. Hg concentration is proportional to the indicated absorbance. A soda-lime trap and a magnesium perchlorate trap must be used to precondition the gas before it enters the absorption cell.

## **Continuous Mercury Monitors**

Four different Hg semicontinuous emission monitors (Hg SCEMs) were used for these tests: the Semtech Hg 2010, PS Analytical (PSA) Sir Galahad, Tekran, and OhioLumex. These instruments, when used in conjunction with the Energy & Environmental Research Center (EERC) or PSA conversion systems, with some caveats as explained in the report, were able to measure speciated Hg. The instruments are briefly described below.

### ***Atomic Fluorescence-Based Hg SCEMs***

The PSA Sir Galahad and the Tekran are fluorescence-based instruments. The Sir Galahad analyzer was initially used to monitor total Hg continuously in the urban environment and natural gas. The Tekran analyzer was initially used to primarily monitor ambient Hg. As was the case for this project, both of these instruments can be used in a variety of gaseous media including combustion flue gas. These analyzers are based on the principle of atomic fluorescence (AF), which provides an inherently more sensitive signal than AA. The systems use a gold-impregnated silica support for preconcentrating the Hg and separating it from potential interferences that degrade sensitivity.

These instruments require a four-step process to obtain a flue gas Hg measurement. In the first step, conditioned flue gas is pumped through a gold trap, which is maintained at a constant temperature. Before the Hg is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present because it has a damping effect on the Hg fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold trap is heated to desorb the Hg from the trap. The Hg is carried into the fluorescence detector in an inert gas stream of argon or nitrogen, depending on the Hg concentration. The gold trap is then cooled in preparation for the next sample. The time for the entire process is about 5 min.

The systems are calibrated using  $\text{Hg}^0$  as the primary standard. The  $\text{Hg}^0$  is contained in a closed vial, which is held in a thermostatic bath. The temperature of the Hg is monitored, and the amount of Hg is measured using vapor pressure calculations. Typically, the calibration of these units has proven to be stable over a 24-hr period.

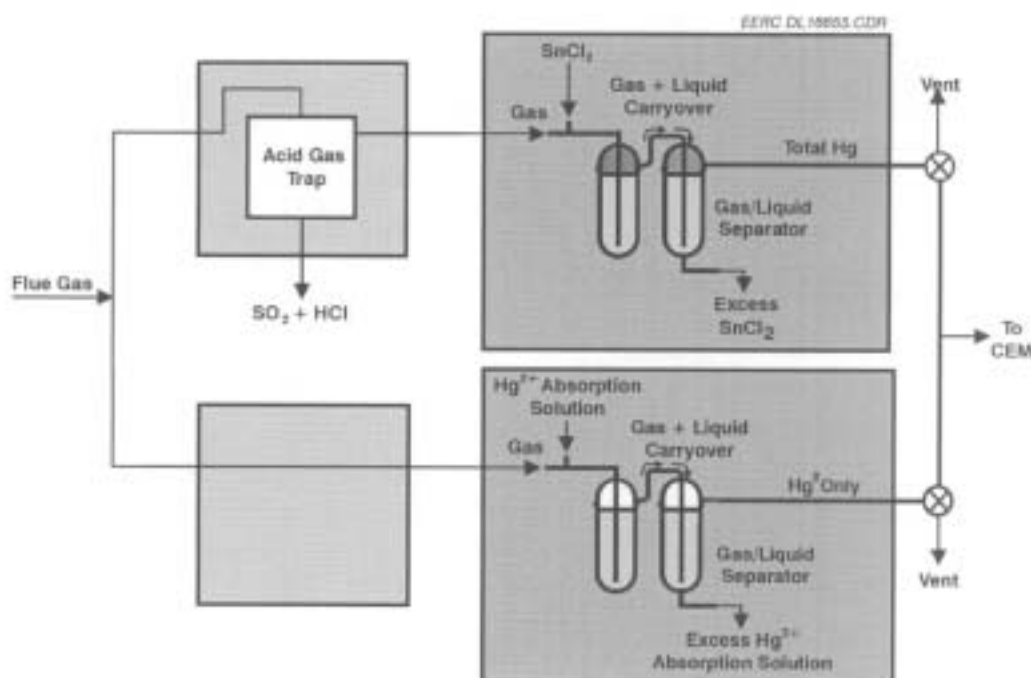
### ***Atomic Absorption-Based Hg SCEMs***

Both the Semtech Hg analyzer (Semtech Metallurgy AB, Lund, Sweden) and the OhioLumex instruments are portable Zeeman-modulated CVAA spectrometers that can monitor  $\text{Hg}^0$  continuously. These analyzers use Zeeman effect background correction by applying a modulated magnetic field to a Hg lamp to minimize interferences from the presence of  $\text{SO}_2$ , moisture, hydrocarbons, and fine particulate in the flue gas sample. The primary difference between the Semtech and the OhioLumex instruments is the AA path length. The Semtech has a path length of about 0.5 m compared to 9.7 m for the OhioLumex. The result is a much lower detection limit for the OhioLumex. The operating range of the Semtech is listed as 0.3 to  $160 \text{ mg/Nm}^3 \text{ Hg}^0$ ; however, in practice, the lower limit of quantification is about  $2 \text{ } \mu\text{g/Nm}^3$ . The OhioLumex has the potential to measure as low as  $0.1 \text{ ng/Nm}^3$ . It should be noted that the

Semtech Hg 2010 has also been certified by TÜV Rheinland for determining compliance with the German legal limit of  $50 \mu\text{g}/\text{Nm}^3$  for total Hg from waste incinerators.

### Flue Gas Pretreatment/Conversion

Whether the Hg SCCEM uses CVAA or AF to measure Hg, some form of gas pretreatment is necessary before accurate measurement of total Hg (or speciated Hg) is obtained. Figure A-3 illustrates the EERC pretreatment system used with Hg SCCEMs. For the CVAA-type systems, only  $\text{Hg}^0$  can be directly analyzed. Therefore, all Hg forms in the flue gas must be converted to  $\text{Hg}^0$ . For this purpose,  $\text{SnCl}_2$  is used as a reductant. To use an Hg SCCEM for Hg speciation measurements, first only  $\text{Hg}^0$  (bypassing the  $\text{SnCl}_2$ ) is measured, followed by a measurement of the total Hg by reducing the  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  with  $\text{SnCl}_2$  prior to analysis. The  $\text{Hg}^{2+}$  concentration was calculated by difference.



**Figure A-3**  
Schematic of the EERC Pretreatment/Conversion System for Use with Hg SCCEMs

For the AF Hg SCCEMs, a pretreatment/conversion system is also needed, but for different reasons. The first reason is to remove gaseous contaminants ( $\text{HCl}$ ,  $\text{SO}_3$ , etc.) from flue gas prior to the gold trap, thus preventing the trap from becoming poisoned permanently. The second reason is that both  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  collect on the trap; if the instrument is to be used to provide Hg speciation data, then the  $\text{Hg}^{2+}$  must be removed from the gas stream so that the  $\text{Hg}^0$  concentration can be measured. To do this, either a heated carbonate trap (the EERC system) or a basic  $\text{SnCl}_2$  trap (PSA system) is used. For all the tests discussed in this report, the PSA system was used.

## Auxiliary Flue Gas Measurements

Auxiliary flue gas measurements were performed using a portable O<sub>2</sub> analyzer (as described below) and H<sub>2</sub>O by EPA Method 4 (condensation/gravimetric analysis). These measurements were collected as integral parts of all Hg speciation tests at all locations.

### O<sub>2</sub> Determination

O<sub>2</sub> is measured by a portable O<sub>2</sub> analyzer using an electrochemical cell. The gas sample for the portable analyzer is drawn through a tube inserted in the exit gas of the sample gas meter. This provides direct analysis of the gas sampled for the Hg test. Care should be taken so that the O<sub>2</sub> sample tube is not inserted so far that it interferes with the meter orifice pressure differential reading. Calibration procedures for the portable analyzer include the following:

- At the beginning of each test condition, the instrument is calibrated on ambient air. As-found readings are then taken using zero gas and a mid-scale O<sub>2</sub> calibration gas (40%–60% of the span to be used to collect readings). If these as-found readings are within 2% of span (0.2% O<sub>2</sub> if the 10% scale is used), the data are acceptable. If the readings are outside of these ranges, the O<sub>2</sub> cell should be replaced, the instrument should be repaired, or an alternate instrument should be used.
- During testing, the calibration of the instrument is checked daily on ambient air. The as-found reading is taken, and the instrument is recalibrated on ambient air.

At the end of the test condition, the calibration error step described above is repeated.

### CO<sub>2</sub> Determination

CO<sub>2</sub> is used for molecular weight determination. At the stack, CO<sub>2</sub> readings are taken from the plant continuous emission monitor (CEM). If the CEM readings are on a wet basis, they are converted to a dry basis using the moisture content measured by the Hg train. If the CEM is out of service or does not provide CO<sub>2</sub> measurements, the CO<sub>2</sub> content is calculated stoichiometrically from a fuel analysis.

### Chlorides, NH<sub>3</sub>, and SO<sub>3</sub>

To measure chloride concentrations in the flue gas, EPA Method 26A was used. This method was designed to measure both the HCl/HF and Cl<sub>2</sub> concentrations in the flue gas. However, when SO<sub>2</sub> was present in the flue gas, it was found that the method only provides total chlorides [1]. The impinger train is operated similarly to other sampling procedures such as EPA Method 5. Once the chlorides are collected in the solutions, they are analyzed using ion chromatography techniques. For SO<sub>3</sub> measurements, the controlled condensation technique was used. For NH<sub>3</sub> analyses, the flue gas is absorbed in 0.1 N HCl solution, and the NH<sub>3</sub> is measured using a selective ion electrode.

## Reference

1. Sun, Q.; Crocker, C.R.; Lillemoen, C.M. The Effect of Coal Combustion Flue Gas Components on Low-Level Chlorine Speciation Using EPA Method. In *Proceedings of the 92nd Annual Meeting & Exhibition of Air & Waste Management Association*; St. Louis, MO, June 20–24, 1999.



# B

## MERCURY MEASUREMENTS

### B.1 Mercury Measurements Made at Site S2

#### Complete OH Data Set

Table B-1  
OH Mercury Data for Site S2 with the SCR in Service

Date	Hours into Test		$\mu\text{g}/\text{Nm}^3$			
	Start	End	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>
<i>SCR Inlet</i>						
07/17/02	58.0	59.2	0.01	7.6	4.8	12.4
07/18/02	85.6	87.6	0.09	5.4	7.5	13.0
07/19/02	106.9	108.9	0.03	6.5	4.2	10.7
Average			0.04	6.5	5.5	12.0
<i>SCR Outlet</i>						
07/17/02	58	58.6	0.14	11.1	3.3	14.6
07/18/02	85.6	87.6	0.03	11.8	0.8	12.6
07/19/02	106.7	108.7	0.02	9.5	0.5	10.1
Average			0.06	10.8	1.6	12.4
<i>ESP Inlet</i>						
07/18/02	90.1	91.6	0.00	12.2	0.5	12.7
07/19/02	110.8	112.3	0.06	12.2	0.2	12.4
Average			0.03	12.2	0.3	12.6
<i>ESP Outlet</i>						
07/18/02	90.8	92.3	0.00	11.3	0.5	11.8
07/19/02	110.9	112.9	0.00	10.9	0.2	11.1
Average			0.00	11.1	0.3	11.5
<i>Stack</i>						
07/18/02	91.2	93.2	0.00	0.5	1.4	1.8
07/20/02	132.9	134.9	0.00	0.9	1.2	2.1
Average			0.00	0.7	1.3	2.0



**Coal Mercury and Chloride Analyses****Table B-2**  
**Coal Analysis Completed at Site S2**

Date	Chloride, ppm	Mercury, ppm
7/15/2002	672	0.10
7/15/2002	733	0.12
7/16/2002	577	0.15
7/16/2002	689	0.11
7/17/2002	724	0.12
7/17/2002	717	0.14
7/18/2002	605	0.11
7/18/2002	605	0.11
7/19/2002	593	0.11
7/20/2002	609	0.13
7/21/2002	635	0.12
7/22/2002	638	0.12
7/23/2002	639	0.12
7/23/2002	686	0.13
7/24/2002	704	0.11
7/24/2002	658	0.12
7/25/2002	601	0.10
7/25/2002	656	0.11
7/26/2002	640	0.11
7/27/2002	650	0.13
7/28/2002	602	0.10
7/28/2002	569	0.14
7/29/2002	640	0.12
7/29/2002	637	0.12
7/30/2002	646	0.14
7/30/2002	655	0.10
7/31/2002	684	0.14
7/31/2002	636	0.15
08/1/2002	710	0.15
08/2/2002	624	0.13
8/03/2002	630	0.10
8/03/2002	570	0.17
8/04/2002	648	0.10
8/04/2002	619	0.11
8/05/2002	561	0.07
8/06/2002	680	0.10
8/06/2002	617	0.10
8/07/2002	600	0.13
8/08/2002	591	0.16
8/09/2002	617	0.11
8/09/2002	621	0.11
8/10/2002	654	0.14
8/10/2002	622	0.14
8/10/2002	582	0.13
8/10/2002	561	0.13
Average	636	0.12
Standard Deviation	44	0.02

## B.2 Mercury Measurements Made at Site S4

### Complete OH Data Set

Table B-3  
OH Mercury Data for Site S4 with the SCR In Service

Date	Hours into Test		$\mu\text{g}/\text{Nm}^3$			
	Start	End	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>
<i>SCR Inlet</i>						
9/11/02	63.8	65.8	0.04	5.6	8.1	13.8
9/12/02	86.9	88.5	0.11	3.0	7.8	10.9
9/13/02	107.7	109.0	0.00	3.2	8.9	12.1
Average			0.05	4.0	8.3	12.3
<i>SCR Outlet</i>						
9/11/02	63.8	64.8	0.01	12.0	3.0	15.1
9/12/02	87.0	88.3	0.00	2.8	4.6	7.4
9/13/02	107.8	108.8	0.00	6.3	5.2	11.5
Average			0.00	7.1	4.3	11.3
<i>AH Outlet</i>						
9/11/02	63.7	65.7	0.03	11.6	0.5	12.2
9/12/02	82.8	84.8	0.06	13.2	0.5	13.7
9/12/02	87.4	89.4	0.10	9.2	0.4	9.6
Average			0.06	11.3	0.5	11.8
<i>Stack</i>						
9/11/02	63.8	65.8	— <sup>a</sup>	0.3	0.7	0.9
9/12/02	82.9	84.4	—	0.3	0.9	1.2
9/12/02	87.9	89.6	—	0.3	0.8	1.2
Average				0.3	0.8	1.1

<sup>a</sup> Not analyzed (all values will be  $<0.1 \mu\text{g}/\text{Nm}^3$ ).

**Table B-4**  
**OH Mercury Data for Site S4 with the SCR Bypassed**

Date	Hours into Test		Hg <sub>p</sub>	μg/Nm <sup>3</sup>		
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>
<i>AH Outlet</i>						
10/16/02	898.0	900.0	0.14	8.3	5.9	14.4
10/16/02	891.5	893.5	0.05	8.0	6.5	14.6
10/17/02	923.0	925.0	0.05	6.8	4.5	11.3
Average			0.08	7.7	5.6	13.4
<i>Stack</i>						
10/16/02	898.3	900.0	— <sup>a</sup>	0.4	6.9	7.2
10/16/02	891.5	893.2	—	0.7	7.2	7.9
10/17/02	923.0	924.7	—	0.3	7.2	7.4
Average				0.5	7.1	7.5

<sup>a</sup> Not analyzed (all values will be <0.1  $\mu\text{g}/\text{Nm}^3$ ).

### B.3 Mercury Measurements Made at Site S5

#### Complete OH Data Set

Table B-5  
OH Mercury Data for Site S5 for Unit with the SCR

Date	Hours into Test		Hg <sub>p</sub>	μg/Nm <sup>3</sup>		Hg <sub>Total</sub>
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	
SCR Inlet						
08/17/02	538.6	540.0	0.16	7.5	5.6	13.3
08/18/02	565.1	566.6	0.08	6.0	8.8	14.9
08/21/02	634.1	635.6	0.04	4.7	9.1	13.8
Average			0.09	6.1	7.8	14.0
SCR Outlet						
08/17/02	538.4	539.9	0.07	11.7	0.6	12.4
08/18/02	565.1	566.6	0.04	10.7	3.3	14.0
08/21/02	634.1	635.6	0.02	10.3	2.4	12.7
08/22/02	665.1	666.6	0.00	15.6	5.1	20.7
08/23/02	686.5	688.0	0.02	10.5	2.3	12.8
Average			0.03	11.8	2.7	14.5
ESP Inlet						
08/21/02	638.8	640.3	0.13	11.7	0.8	12.6
08/22/02	665.3	666.8	0.00	18.4	1.0	19.4
08/23/02	689.0	690.5	0.09	20.2	0.5	20.8
Average			0.07	16.8	0.8	17.7
ESP Outlet						
07/26/02	12.1	14.1	0.09	11.7	0.6	12.4
07/27/02	38.3	40.3	0.25	8.2	0.6	9.1
07/28/02	57.3	59.3	0.01	7.7	0.9	8.6
08/15/02	493.9	495.4	0.03	14.2	0.6	14.8
08/17/02	543.0	544.5	0.01	10.7	0.6	11.3
08/19/02	590.0	591.5	0.00	8.7	0.6	9.3
08/21/02	637.4	638.9	0.00	10.4	0.9	11.3
08/22/02	665.3	666.8	0.01	19.1	0.9	20.0
Average			0.05	11.3	0.7	12.1
Stack						
08/17/02	543.6	545.1	0.03	0.4	0.8	1.2
08/21/02	637.5	639.0	0.01	0.4	1.2	1.6
Average			0.02	0.4	1.0	1.4

**Table B-6**  
**OH Mercury Data for Site S5 for Unit Without an SCR**

Date	Hours into Test		Hg <sub>p</sub>	μg/Nm <sup>3</sup>		
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>T</sub>
ESP Inlet						
08/13/02	446.3	447.8	0.01	10.7	1.4	12.1
08/14/02	472.2	473.7	0.10	11.7	2.8	14.7
08/16/02	515.8	517.3	0.03	10.1	3.7	13.8
Average			0.05	10.8	2.6	13.5
ESP Outlet						
07/26/02	11.4	13.4	0.02	8.7	4.1	12.8
07/27/02	38.3	40.3	0.03	7.1	4.2	11.3
07/28/02	57.2	59.2	0.01	5.6	4.4	10.0
08/13/02	446.3	447.8	0.00	8.1	5.8	13.8
08/14/02	472.2	473.7	0.00	9.4	5.1	14.5
08/16/02	515.8	517.3	0.00	7.1	6.0	13.1
08/23/02	682.8	684.3	0.01	9.5	3.1	12.6
Average			0.01	7.9	4.7	12.6
Stack						
08/13/02	446.1	447.6	0.00	0.4	6.7	7.1
08/14/02	473.3	474.4	0.01	0.7	5.9	6.5
08/15/02	494.0	495.5	0.00	0.4	5.6	6.0
Average			0.00	0.5	6.1	6.6

**Table B-7**  
**Coal Mercury and Chloride Analyses**

Date	Chloride, ppm	Mercury, ppm
07/26/2002	450	0.14
07/28/2002	430	0.14
08/01/2002	440	0.14
08/05/2002	500	0.12
08/13/2002	500	0.13
08/15/2002	480	0.15
08/19/2002	490	0.13
08/21/2002	460	0.15
08/23/2002	500	0.11
Average	472	0.13
Standard Deviation	28	0.013

## B.4 Mercury Measurements Made at Site S6

### Complete OH Data Set

Table B-8  
OH Mercury Data for Site S6 for Unit 1 (SCR)

Date	Hours into Test		Hg <sub>p</sub>	μg/Nm <sup>3</sup>		Hg <sub>Total</sub>
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	
SCR Inlet						
09/24/02	81.9	83.5	0.03	4.1	3.0	7.2
09/25/02	106.0	107.2	0.05	6.7	4.0	10.7
09/26/02	129.1	130.6	— <sup>a</sup>	5.5	3.8	9.2
09/26/02	133.3	135.3	—	7.0	4.1	11.1
Average			0.04	5.8	3.8	9.0
SCR Outlet						
09/24/02	82.0	83.5	0.03	5.5	1.1	6.7
09/25/02	106.0	107.2	0.04	7.7	1.6	9.4
09/26/02	129.1	130.6	—	6.6	1.8	8.3
09/26/02	133.3	135.3	0.01	8.5	1.6	10.2
Average			0.03	7.1	1.5	8.6
ESP Inlet						
09/24/02 <sup>b</sup>	85.8	86.3	—	2.1	0.9	3.1
09/24/02	87.4	88.9	0.95	9.9	0.3	11.2
09/25/02	109.9	111.3	0.70	7.3	0.7	8.7
09/26/02	129.1	130.6	0.75	8.3	0.4	9.4
Average			0.80	8.5	0.5	9.8
Stack						
09/22/02	40.0	42.0	—	6.0	0.2	6.2
09/23/02	62.8	64.3	—	8.9	0.4	9.3
09/24/02	85.8	87.3	—	14.3	0.5	14.9
09/25/02	109.8	111.3	0.00	8.3	1.2	9.5
09/26/02	129.1	130.6	—	7.5	1.5	9.0
10/08/02	424.8	426.3	—	11.8	0.7	12.6
10/11/02	497.0	498.5	—	10.6	0.5	11.1
10/12/02	518.0	520.0	—	8.2	0.2	8.4
10/13/02	542.0	543.5	0.01	9.0	0.2	9.3
10/14/02	564.0	566.0	—	8.0	0.6	8.7
10/17/02	636.5	638.5	—	10.6	0.2	10.8
10/18/02	661.7	663.7	—	8.0	3.4	11.3
Average			0.00	9.3	0.8	10.1

<sup>a</sup> Not analyzed (all values will be <0.1 μg/Nm<sup>3</sup>).

<sup>b</sup> Bold values not included in averages as there was a problem that occurred during sampling.

**Table B-9**  
**OH Mercury Data for Site S6 for Unit 2 (SCR bypassed)**

Date	Hours into Test		Hg <sub>P</sub>	$\mu\text{g}/\text{Nm}^3$		
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>
ESP Inlet						
10/08/02	425.2	426.5	3.74	6.0	0.5	10.2
10/12/02	518.0	519.5	1.44	7.1	0.3	8.8
10/18/02 <sup>a</sup>	657.8	659.3	9.16	1.0	0.1	10.3
Average			2.59	6.6	0.4	9.5
Stack						
09/22/02 <sup>b</sup>	39.8	41.8	— <sup>c</sup>	6.6	0.0	6.6
09/23/02	63.3	64.8	—	7.1	0.2	7.3
09/25/02	110.2	111.7	0.00	7.9	0.6	8.5
10/08/02	424.8	426.8	—	7.2	1.4	8.6
10/11/02	497.3	498.8	—	4.6	0.8	5.4
10/12/02	518.0	520.0	—	6.5	1.5	8.0
10/13/02	542.0	543.5	0.01	6.0	1.7	7.7
10/14/02	564.0	566.0	—	5.5	1.5	7.0
10/17/02	636.6	638.6	—	5.3	1.2	6.5
10/18/02	661.7	663.7	—	6.8	0.8	7.7
Average			0.01	6.0	1.3	7.3
Standard Dev.			0.01	0.9	0.4	1.1

<sup>a</sup> Bold values not included in averages as sample appears to be a clear outlier.

<sup>b</sup> Data from 9/22 through 9/25/02 was collected prior to the SCR being bypassed for this unit and are not included in the averages.

<sup>c</sup> Not analyzed (all values will be <0.1  $\mu\text{g}/\text{Nm}^3$ ).



**Table B-10**  
OH Mercury Data for Site S6 for Unit 4 (no SCR)

Date	Hours into Test		Hg <sub>P</sub>	μg/Nm <sup>3</sup>		
	Start	End		Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>
Stack						
10/08/02	424.7	426.2	— <sup>a</sup>	5.8	2.1	7.9
10/11/02	497.3	498.8	—	4.6	1.1	5.7
10/12/02	518.0	520.0	0.00	4.4	1.2	5.6
10/13/02	542.0	543.5	0.02	3.5	1.8	5.4
10/14/02	564.0	566.0	—	2.0	2.0	4.0
10/17/02	636.5	638.5	—	4.1	2.2	6.2
10/18/02	661.7	663.7	—	3.4	2.2	5.6
Average			0.01	4.0	1.8	5.8

<sup>a</sup> Not analyzed (all values will be <0.1  $\mu\text{g}/\text{Nm}^3$ ).

**Table B-11**  
Coal Mercury and Chloride Analyses for Site S6

Date	Unit Collected	Chloride, ppm	Mercury, ppm
09/24/2002	1 (SCR)	1210	0.084
09/24/2002	2 (SCR bypassed)	1520	0.052
09/26/2002	1 (SCR)	871	0.072
09/26/2002	2 (SCR bypassed)	635	0.055
10/08/2002	1 and 2 <sup>a</sup>	1170	0.063
10/08/2002	4 (no SCR)	1320	0.066
10/12/2002	1 and 2 <sup>a</sup>	962	0.069
10/18/2002	1 (SCR)	794	0.070
10/18/2002	4 (no SCR)	706	0.064
Average		1020	0.066
Standard Deviation		300	0.0094

<sup>a</sup> Composite sample from Units 1 and 2.

# C

## COMPLETE AUXILIARY FLUE GAS DATA FOR ALL SITES

Table C-1  
Auxiliary Flue Gas Data for Site S2 with SCR in Service

Date	Time into the Test, hr	Flue Gas Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>SCR Inlet</i>					
07/17/02	58.0	9.97	0.1609 <sup>b</sup>	14.8	3.7
07/18/02	85.6	9.57	3.2881	15.1	3.8
07/19/02	106.9	9.79	2.2725	15.0	3.9
Average		9.77	2.7803	15.0	3.8
<i>SCR Outlet</i>					
07/17/02	58.0	11.00	3.2452	14.8	4.6
07/18/02	85.6	10.79	0.8248 <sup>a</sup>	14.8	4.8
07/19/02	106.7	10.71	3.4642	14.8	4.4
Average		10.83	3.3547	14.8	4.6
<i>ESP Inlet</i>					
07/18/02	90.1	11.36	0.0385 <sup>a</sup>	13.8	5.6
07/19/02	110.8	11.15	1.8872	13.9	5.8
Average		11.25	1.8872	13.9	5.7
<i>ESP Outlet</i>					
07/18/02	90.8	11.40	0.0024	13.7	5.8
07/19/02	110.9	10.54	0.0018	13.7	5.8
Average		10.97	0.0021	13.7	5.8
<i>Stack</i>					
07/18/02	91.2	17.45	0.0008	13.3	6.4
07/20/02	132.9	26.25	0.0025	13.1	6.5
Average		21.85	0.0016	13.2	6.5

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

<sup>b</sup> Dust loadings are lower than expected, attributed to ash loss upon removal of probe and single-point sampling, and not included as part of the average.

**Table C-2**  
**Auxiliary Flue Gas Data for Site S4 with SCR in Service**

Date	Time into Test, hr	Flue Gas Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>SCR Inlet</i>					
9/11/2002	63.8	9.5	1.3396	15.5	3.5
9/12/2002	86.9	9.6	2.1084	14.3	4.6
9/13/2002	107.7	11.3	2.3317	15.3	3.5
Average		10.1	1.9266	15.0	3.9
<i>SCR Outlet</i>					
9/11/2002	63.8	8.6	2.7819	15.1	3.7
9/12/2002	87.0	14.0	4.0879	14.5	4.4
9/13/2002	107.8	10.3	2.7819	15.1	3.6
Average		10.9	3.2172	14.9	3.9
<i>Air Preheater Outlet</i>					
9/11/2002	63.7	8.6	1.2303	13.4	5.5
9/12/2002	82.8	8.3	1.2135	13.0	6.0
9/12/2002	87.4	9.0	0.8638	11.2	8.0
Average		8.6	1.1025	12.5	6.5
<i>Stack</i>					
9/11/2002	63.8	15.7	0.0000	11.8	7.4
9/12/2002	82.9	17.3	0.0000	11.4	7.9
9/12/2002	87.9	12.6	0.0000	11.3	8.0
Average		15.2	0.0000	11.5	7.8

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

**Table C-3**  
**Auxiliary Flue Gas Data for Site S4 with SCR Bypassed**

Date	Time into Test, hr	Flue Gas Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
Air Preheater Outlet					
10/16/2002	898.0	10.2	1.2291	11	8.0
10/16/2002	891.5	8.2	0.9940	11	8.0
10/17/2002	923.0	8.3	1.4883	11.2	7.8
Average		8.9	1.2371	11.1	7.9
Stack					
10/16/2002	898.3	15.4	0.0084	11.2	7.8
10/16/2002	891.5	12.3	0.0032	11.1	7.9
10/17/2002	963.0	14.1	0.0080	11.1	7.9
Average		13.9	0.0065	11.1	7.9

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

**Table C-4**  
**Auxiliary Flue Gas Data for Site S5 for the Unit with an SCR**

Date	Time into Test, hr	Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
SCR Inlet					
08/17/02	538.6	10.68	16.2456	14.7	4.7
08/18/02	565.1	10.83	6.5134	13.9	5.6
08/21/02	634.1	10.45	3.5652	14.2	4.7
Average		10.65	8.7747	14.3	5.0
SCR Outlet					
08/17/02	538.4	9.51	4.6314	14.3	5.1
08/18/02	565.1	9.37	3.7380	13.1	6.5
08/21/02	634.1	8.31	3.0199	13.4	6.0
08/22/02	665.1	9.48	2.3088	14.0	5.5
08/23/02	686.5	8.63	3.3436	14.0	5.5
Average		9.06	3.4083	13.8	5.7
ESP Inlet					
08/21/02	638.8	8.67	2.1219	12.9	6.8
08/22/02	665.3	9.26	1.7475	13.2	6.4
08/23/02	689.0	8.73	1.1852	13.2	6.4
Average		8.89	1.6848	13.1	6.5
ESP Outlet					
07/26/02	12.1	9.30	0.0739	13.0	6.6
07/27/02	38.3	8.94	0.1573	13.2	6.4
07/28/02	57.3	9.08	0.0669	13.2	6.4
08/15/02	493.9	8.90	0.1726	13.3	6.3
08/17/02	543.0	9.27	0.0284	12.2	7.4
08/19/02	590.0	6.79	0.0082	12.2	7.4
08/21/02	637.4	8.57	0.0521	12.7	7.0
08/22/02	665.3	8.95	0.0412	13.6	5.9
Average		8.73	0.0751	12.9	6.7
Stack					
08/17/02	543.6	13.88	0.0061	11.7	8.0
08/21/02	637.5	12.26	0.0085	12.0	7.5
Average		13.07	0.0073	11.9	7.8

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

**Table C-5**  
**Auxiliary Flue Gas Data for Site S5 for the Unit Without an SCR**

Date	Time into Test, hr	Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>ESP Inlet</i>					
08/13/02	446.3	8.3	0.2117	13.6	6.0
08/14/02	472.2	8.1	1.8369	13.8	6.0
08/16/02	515.8	9.3	0.4373	13.3	6.3
Average		8.7	0.8287	13.6	6.1
<i>ESP Outlet</i>					
07/26/02	11.4	9.1	0.0711	12.8	6.8
07/27/02	38.3	9.1	0.1078	13.3	6.3
07/28/02	57.2	8.9	0.0487	13.3	6.3
08/13/02	446.3	8.5	0.0091	13.0	6.6
08/14/02	472.2	8.1	0.0259	12.9	6.7
08/16/02	515.8	8.9	0.0130	12.4	7.2
08/23/02	682.8	10.7	0.0419	12.4	7.2
Average		9.0	0.0453	12.9	6.7
<i>Stack</i>					
08/13/02	446.1	13.6	0.0034	12.8	6.9
08/14/02	473.3	13.2	0.0111	12.7	7.0
08/15/02	493.8	13.6	0.0045	12.7	7.0
Average		13.5	0.0063	12.7	7.0

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

**Table C-6**  
**Auxiliary Flue Gas Data for Site S6 for Unit 1 (SCR)**

Date	Time into Test, hr	Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>SCR Inlet</i>					
09/24/02	27.4	9.04	3.4195	15.2	4.1
09/25/02	28.4	9.01	3.7122	13.4	6.1
09/26/02	29.4	9.03	4.2123	15.2	4.2
09/26/02	29.6	8.98	3.5784	15.0	4.4
Average		9.01	3.7306	14.7	4.7
<i>SCR Outlet</i>					
09/24/02	27.4	8.36	3.7555	15.1	4.3
09/25/02	28.4	8.89	3.7580	15.2	4.1
09/26/02	29.4	8.74	5.1397	15.4	3.9
09/26/02	29.6	8.94	4.0159	15.2	4.2
Average		8.73	4.1673	15.2	4.1
<i>ESP Inlet</i>					
09/24/02	27.6	10.51	0.4491	13.4	4.7
09/24/02	27.6	8.82	3.1538	13.4	4.7
09/25/02	28.6	8.05	2.1157	13.9	5.6
09/26/02	29.4	8.33	5.2099	14.4	5.0
Average		8.93	2.7321	13.8	5.0
<i>Stack</i>					
09/22/02	25.7	10.09	0.0111	13.5	6.0
09/23/02	26.6	9.62	0.0076	13.3	6.3
09/24/02	27.6	9.69	0.0059	13.4	6.2
09/25/02	28.6	9.17	0.0213	13.0	6.6
09/26/02	29.4	9.49	0.0074	13.5	6.0
10/08/02	41.7	9.64	0.0053	12.8	6.8
10/11/02	44.7	10.15	0.0044	12.8	6.8
10/12/02	45.6	9.76	0.0210	13.2	6.4
10/13/02	46.6	9.11	0.0335	12.9	6.7
10/14/02	47.5	8.65	0.0291	12.8	6.8
10/17/02	50.5	8.45	0.0292	12.5	7.1
10/18/02	51.6	8.29	0.0221	13.2	6.4
Average		9.34	0.0165	13.1	6.5

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

**Table C-7**  
**Auxiliary Flue Gas Data for Site S6 for Unit 2 (SCR bypassed)**

Date	Time into Test, hr	Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>ESP Inlet</i>					
10/08/02	41.7	9.10	4.0591	15.4 <sup>b</sup>	3.5
10/12/02	45.6	9.34	3.2689	15.4	3.9
10/18/02	51.4	7.72	4.8572	15.4 <sup>b</sup>	3.7 <sup>b</sup>
10/18/02	51.5	6.95	4.7264	15.4 <sup>b</sup>	3.7 <sup>b</sup>
Average		8.28	4.2279	15.4	3.7
<i>Stack</i>					
09/22/02	25.7	8.56	0.0118	13.2	6.4
09/23/02	26.6	8.32	0.0119	12.8	6.8
09/25/02	28.6	7.59	0.0080	13.4	6.2
10/08/02	41.7	7.82	0.0068	13.4	6.1
10/11/02	44.7	8.42	0.0082	13.3	6.3
10/12/02	45.6	8.20	0.0039	13.2	6.4
10/13/02	46.6	7.59	0.0254	13.1	6.5
10/14/02	47.5	7.05	0.0237	12.9	6.7
10/17/02	50.5	6.97	0.0148	13.1	6.5
10/18/02	51.6	7.18	0.0349	13.2	6.4
Average		7.77	0.0150	13.2	6.4

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

<sup>b</sup> Invalid data: average was used.



**Table C-8**  
**Auxiliary Flue Gas Data for Site S6 for Unit 4 (no SCR)**

Date	Time into Test, hr	Moisture, %	Dust Loading, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
Stack					
10/08/02	41.7	7.82	0.0460	14.3	5.2
10/11/02	44.7	8.93	0.0022	14.5	4.9
10/12/02	45.6	8.52	0.0265	14.8	4.6
10/13/02	46.6	7.95	0.0587	14.7	4.7
10/14/02	47.5	7.28	0.0463	14.5 <sup>b</sup>	4.9 <sup>b</sup>
10/17/02	50.5	6.87	0.0521	14.7	4.7
10/18/02	51.6	6.99	0.0398	14.3	5.2
Average		7.77	0.0388	14.5	4.9

<sup>a</sup> Dust loadings were collected as part of the OH testing using the EPA Method 17 procedure and, therefore, are not for compliance purposes.

<sup>b</sup> Invalid data: average was used.

# **D**

## **QUALITY ASSURANCE/QUALITY CONTROL**

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This appendix provides detailed quality assurance/quality control (QA/QC) procedures that were used for the sampling activities. The most important QA/QC parameter for any sampling activity is the people who perform the work. All who participated in the sampling activities for this project had extensive training and experience in the proper procedures.

### **Ontario Hydro (OH) Method**

To provide a high level of QA/QC for this project, all liquid samples (from the OH mercury [Hg] speciation train impingers as outlined in Appendix A), including those used as blanks and spikes, were analyzed on-site by the Energy & Environmental Research Center (EERC). The primary advantage of on-site analysis is that Hg analyses can usually be obtained within 24 hr after the sampling. So if there is a problem, it can be corrected when the sampling people are on-site. The following are specific QC procedures for the OH sampling.

#### ***Instrument Setup and Calibration***

A Leeman Labs PS200 cold-vapor atomic absorption instrument was used in the field for Hg determination. The instrument was set up for absorption at 253.7 nm, with a carrier gas of nitrogen and 10% SnCl<sub>2</sub> in 10% HCl as the reductant. Each day, the drying tube and acetate trap were replaced, and the tubing was checked. The rinse container was then cleaned and filled with a fresh solution of 10% HCl. After the pump and lamp were turned on and warmed up for 45 min, the aperture was set to the manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This QC standard was prepared from a different stock than the calibration standards. Requirements stated that the values obtained must read within 5% of the true value before the instrument was used. After the initial QC standardization was completed, standards were run every ten samples to check the slope of the calibration curve. One in every ten samples was run in triplicate and spiked to verify analyte recovery. A QC chart was also maintained by the EERC chemist to monitor the long-term precision of the instrument.

### ***Presampling Preparation***

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks, logged, and then analyzed on-site. The stack filter samples were placed in premarked petri dishes, then taken back to the EERC, where they were analyzed using mixed-acid digestion techniques. The prestack filter samples were placed in premarked containers, logged, and then analyzed on-site using a Milestone DMA-80 instrument. The labels contained identifying data, including date, time, run number, and sample port location, which correlate back to the data sheets.

### ***Glassware and Plasticware Cleaning and Storage***

All glass volumetric flasks and transfer pipettes used in the preparation of analytical reagents and calibration standards were designated as "Class A" to meet American Society for Testing and Materials specifications. Prior to being used for the sampling, all glassware was washed with hot soapy water, then rinsed with deionized water three times, then soaked in 10%  $\text{v/v}$  nitric acid for a minimum of 4 hr, then rinsed an additional three times with deionized water, and dried. The glassware was stored in closed containers until it was used at the plant.

### ***Analytical Reagents***

All acids used for the analysis of Hg were trace metal-grade. Other chemicals used in the preparation of analytical reagents were analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within  $\pm 0.5\%$  and traceable to National Institute of Standards and Technology Standard Reference Materials.

### ***Blanks and Spikes***

As part of the QA/QC, a field blank was associated with sampling at each location. A field blank is a complete impinger train including all glassware and solutions that is taken out to the field during sampling and exposed to ambient conditions. These sample trains were then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank showed contamination above instrument background levels, steps were then taken to eliminate or reduce the contamination to below background levels.

As part of the QA/QC, a field spike was also associated with each test condition. A field spike was prepared by the field manager at a level similar to the field samples. These sample trains were then taken apart, and the solution was recovered and analyzed in the same manner as those sample trains used for sampling activities. The target range for recovery of the field spike was  $\pm 20\%$ .

The results of the blanks and spikes associated with each of the test sites are shown in Tables D-1–D-7. With very few exceptions, blanks were at or near detection limits and results of the spiked samples were within the 20% range required by the method.

**Table D-1**  
**Results of Mercury Speciation Field Blanks at Site S2**

Date	KCl Solution, $\mu\text{g}$	H <sub>2</sub> O <sub>2</sub> Solution, $\mu\text{g}$	KMnO <sub>4</sub> Solution, $\mu\text{g}$
7/17/2002	0.04	<0.01	<0.01
7/18/2002	0.20	<0.01	0.37
7/19/2002	0.04	<0.01	0.09
7/20/2002	0.03	<0.01	0.05

**Table D-2**  
**Results of Mercury Speciation Field Spikes at Site S2**

Date	KCl			H <sub>2</sub> O <sub>2</sub> Solution			KMnO <sub>4</sub> Solution		
	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
7/17/2002	9.95	10	99.51	0.96	1	96.05	8.49	10	84.85
7/17/2002	4.75	5	94.98	1.06	1	106.25	5.12	5	102.30
7/17/2002	9.37	10	93.69	2.13	2	106.51			
7/18/2002	10.92	10	109.20	1.04	1	103.60	5.02	5	100.40
7/18/2002	4.90	5	98.00	1.04	1	103.95	4.90	5	98.00
7/18/2002	9.80	10	98.00	2.24	2	112.18			
7/19/2002	9.46	10	94.64	1.02	1	101.89	4.98	5	99.60
7/19/2002	4.45	5	89.04	1.14	1	113.78	4.75	5	95.00
7/19/2002	9.02	10	90.16	2.33	2	116.75			

**Table D-3**  
**Results of Mercury Speciation Field Spikes at Site S4<sup>a</sup>**

Date	Measured Value, ppb	KCl		KMnO <sub>4</sub> Solution		
		Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
9/11/2002	9.94	10	99.40	9.00	10	90.00
9/12/2002	9.65	10	96.50	9.53	10	95.30
9/13/2002	9.76	10	97.60	9.46	10	94.60

<sup>a</sup> Sampling at Site S4 was done by Western Kentucky University.

**Table D-4**  
**Results of Mercury Speciation Field Blanks at Site S5**

Date	KCl Solution, $\mu\text{g}$	H <sub>2</sub> O <sub>2</sub> Solution, $\mu\text{g}$	KMnO <sub>4</sub> Solution, $\mu\text{g}$
7/26/2002	0.18	<0.01	0.05
7/27/2002	0.05	0.01	0.08
7/28/2002	0.10	0.09	0.13
8/14/2002	0.04	<0.01	0.06
8/15/2002	0.05	<0.01	0.12
8/18/2002	0.06	<0.01	0.05
8/22/2002	<0.01	0.09	0.01

**Table D-5**  
**Results of Mercury Speciation Field Spikes at Site S5**

Date	KCl			H <sub>2</sub> O <sub>2</sub> Solution			KMnO <sub>4</sub> Solution		
	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
7/26/2002	11.00	10	109.99	0.92	1	92.05	4.48	5	89.60
7/26/2002	5.24	5	104.83	0.81	1	81.20	4.69	5	93.80
7/26/2003	10.00	10	100.01	1.92	2	96.08			
7/27/2002	9.46	10	94.62	0.99	1	99.10	4.96	5	99.20
7/27/2002	4.82	5	96.37	1.98	2	99.10	4.73	5	94.60
7/27/2002	9.30	10	92.98						
7/28/2002	9.75	10	97.48	0.81	1	80.96	4.59	5	91.74
7/28/2002	4.39	5	87.85	0.87	1	86.72	5.13	5	102.60
7/28/2002	9.01	10	90.12	1.97	2	98.72			
8/14/2002	10.15	10	101.49	1.72	2	86.10	5.11	5	102.10
8/14/2002	5.53	5	110.63	2.00	2	99.90	4.75	5	94.90
8/14/2002	9.87	10	98.71	4.76	5	95.14			
8/15/2002	9.21	10	92.06	1.08	1	108.15	5.25	5	104.90
8/15/2002	7.03	7	100.48	1.13	1	112.65	5.16	5	103.10
8/15/2002	11.23	10	112.34	2.31	2	115.43			
8/18/2002	15.64	15	104.24	1.06	1	106.19	7.56	7	108.00
8/18/2002	10.61	10	106.14	0.87	1	86.92	7.84	8	98.00
8/18/2002	15.71	15	104.76	1.75	2	87.33			
8/21/2002	16.52	15	110.13	1.02	1	101.79	6.88	7	98.27
8/21/2002	16.52	15	110.13	1.21	1	121.29	10.62	10	106.21
8/21/2002	21.84	20	109.20	2.08	2	104.13			

**Table D-6**  
**Results of Mercury Speciation Field Blanks at Site S6**

Date	KCl Solution, $\mu\text{g}$	H <sub>2</sub> O <sub>2</sub> Solution, $\mu\text{g}$	KMnO <sub>4</sub> Solution, $\mu\text{g}$
9/23/2002	0.02	<0.01	0.12
9/24/2002	0.11	<0.01	0.15
9/26/2002	0.23	0.07	0.19
9/27/2002	0.04	<0.01	0.10
10/9/2002	0.05	<0.01	0.04
10/13/2002	0.03	0.01	<0.01
10/14/2002	<0.01	<0.01	<0.01
10/15/2002	0.11	0.11	0.09
10/18/2002	0.01	0.02	0.02
10/19/2002	<0.01	0.04	<0.01



**Table D-7**  
**Results of Mercury Speciation Field Spikes at Site S6**

Date	KCl			H <sub>2</sub> O <sub>2</sub> Solution			KMnO <sub>4</sub> Solution		
	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
9/23/2002	10.68	10	106.79	0.83	1	82.93	5.15	5	103.01
9/23/2002	5.56	5	111.22	1.13	1	113.31	5.55	5	110.99
9/23/2002	10.46	10	104.61	2.12	2	106.10			
9/26/2002	3.23	3.4	94.96	1.04	1	103.89	12.47	11.6	107.47
9/26/2002	4.56	5	91.11	0.96	1	96.43	5.63	5	112.67
9/26/2002	10.13	10	101.27	1.58	2	78.93			
9/27/2002	12.42	11.6	107.09	0.97	1	96.75	5.31	5	106.13
9/27/2002	5.50	5	109.96	0.96	1	95.89	5.69	5	113.87
9/27/2002	11.10	10	110.98	1.75	2	87.63			
10/9/2002	4.35	5	87.02	0.88	1	87.73	4.57	5	91.36
10/9/2002	5.39	5	107.86	0.90	1	89.90	5.28	5	105.64
10/9/2002	10.91	10	109.09	1.86	2	93.16			
10/13/2002	4.76	5	95.26	0.89	1	89.33	4.91	5	98.20
10/13/2002	4.56	5	91.22	1.05	1	105.07	5.06	5	101.20
10/13/2002	11.06	10	110.57	1.94	2	96.94			
10/14/2002	5.68	5	113.68	1.05	1	104.81	5.20	5	103.90
10/14/2002	6.10	5	122.08	1.16	1	115.55	5.21	5	104.10
10/14/2002	11.82	10	118.16	2.34	2	116.99			
10/15/2002	4.98	5	99.69	1.18	1	118.20	4.68	5	93.62
10/15/2002	5.36	5	107.23	1.10	1	109.95	5.05	5	100.98
10/15/2002	10.98	10	109.76	1.98	2	98.85			
10/18/2002	5.41	5	108.28	1.39	1	138.56	5.35	5	107.08
10/18/2002	5.55	5	110.96	1.23	1	122.90	5.45	5	108.92
10/18/2002	11.11	10	111.06	2.18	2	109.22			
10/19/2002	5.58	5	111.58	1.64	1	163.57	6.09	5	121.76
10/19/2002	6.15	5	123.06	1.20	1	119.94	5.71	5	114.24
10/19/2002	11.08	10	110.81	2.53	2	126.47			

## **QA/QC Checks for Data Reduction and Validation**

### ***Data Reduction***

Data reduction occurred in two phases. First, preliminary data reduction occurred on the job site. On-site data reduction may be performed by sampling and analytical personnel or by the team leaders. Preliminary calculations include velocity, moisture, stack gas flow, sample gas volume, percent-isokinetic sampling, and flue gas Hg concentrations. Calculations were performed using spreadsheets on a portable computer; some averaging was done with a calculator. Standardized spreadsheets were used.

The second phase of data reduction occurred after the team had left the job site. This included review of the field data and input of laboratory results to complete the calculated Hg concentrations for the coal and ash samples. In addition, the Hg speciation calculations that were done in the field were rechecked and put into a predefined data sheet. Equations to be used in the calculations were contained in the method.

### ***Data Validation***

All data, data entry, and calculations were double-checked by the originator and reviewed by a second person. Reviews included recalculation of results, data entry checks, and calculation of known and accepted data sets using the existing spreadsheet.

## **Sample Identification and Chain of Custody**

Samples were identified with unique sample numbers and descriptive notations. Sample custody was maintained by EERC personnel; samples were stored and taken back to the EERC. Once the samples were received by the EERC laboratory, sample condition was checked and then logged into the EERC logging system.

Data sheets were kept in the custody of the originator or the program manager or in locked storage until returned to the office. The original data sheets were used for report preparation, and any additions were initialed and dated.

## **Personnel Responsibilities and Test Schedule**

### ***Test Site Organization***

Each project comprised a team of personnel able to provide the expertise needed for project completion. The site-specific test plan (SSTP) that was provided to the company outlines the designated management, sampling, and plant personnel required for each project. The key roles of EERC project personnel for project completion are listed below:

- Project manager
- Field manager
- Principal investigator
- Project chemist
- Sample custodian
- Sampling technicians
- Mercury semicontinuous emission monitor (Hg SCCEM) technicians

## **Test Preparations**

### ***Construction of Special Sampling Equipment and Modifications to the Facility***

The correct length of sample probes was made prior to going into the field. No modifications were needed.

### ***General Services Provided by the Facility***

The facility provided safe access to suitable sample ports; process data; 110-V, 20-amp power at the sample locations; a suitable location to park test trailers; and power for the test trailers. In addition, the plant provided restrooms and a clean area for breaks or lunch. The facility was expected to provide the necessary safety training for the sampling team once they were on-site.

### ***Access to Sampling Sites***

Site visits were conducted to determine, among other things, that all sample ports were readily accessible. In addition, measurements were taken so that modifications to probes could be made prior to going into the field.

### ***Sample Recovery Areas***

The EERC provided test trailers to set up and tear down sample trains and do the analysis. The trailers were situated in an area as free as possible from ambient dust contamination.

## **Test Personnel Responsibilities and Detailed Schedule**

Table D-8 lists the key project personnel for this project. Table D-9 lists the various personnel roles and their specific responsibilities. Table D-10 presents a typical test schedule for a 4-week project. A tentative project schedule with dates and activities was provided in the SSTP provided to the company prior to sampling.

**Table D-8**  
**Key Project Personnel**

Organization	Individual	Responsibility	Phone Number	E-Mail Address
EPRI	Paul Chu	EPRI Project Manager	(650) 855-2812	pchu@epri.com
DOE	Lynn Brickett	DOE Performance Monitor	(412) 386-6574	lynn.brickett@netl.doe.gov
EPA	C.W. Lee	Project Consultant	(919) 541-7663	lee.chun-wai@epamail.epa.gov
EERC	Dennis Laudal	Project Manager	(701) 777-5138	dlaudal@undeerc.org
EERC	Jeff Thompson	Principal Investigator	(701) 777-5245	jthompson@undeerc.org
WKU	Wei-Ping Pan	Project Manager	(270) 780-2532	wei-ping.pan@wku.edu
WKU	Kunlei Liu	Principal Investigator	(270)-745-3251	kunlei.liu@wku.edu
QA/QC	David Brekke	QA/QC Manager	(701) 777-5154	dbrekke@undeerc.org
EERC	Jeff Thompson	QA/QC Oversight for WKU	(701) 777-5245	jthompson@undeerc.org

**Table D-9**  
**Test Personnel and Responsibilities**

<b>Staff Assignment</b>	<b>Responsibilities</b>
Project Manager	EPRI, EPA, DOE, and the EERC developed and approved the overall test program, coordinated all test activities, developed the QA/QC test plan, ensured the project was being completed within budgetary guidelines, provided data interpretation and completed all reporting requirements, maintained communication between all test participants, and assisted with other activities as required.
Principal Investigator	Worked with the project manager to coordinate all test activities, was responsible for maintaining communications between the plant representative and the sampling team, provided input into program decisions made by the funding agencies and the project manager, worked with the field manager to ensure that the objectives for each test program were completed, collected plant data, completed data reduction and provided input into all reports, and assisted in other activities as required.
Field Manager	Coordinated or helped perform all sampling activities; coordinated sampling activities being conducted by the EERC with those being conducted by plant personnel; maintained sample custody records; ensured that sampling was completed so that the objectives of the project were met, including all QA/QC requirements; ensured that all safety requirements were met by the sampling team; provided input into project reports; and assisted other activities as required.
Team Leader	Prepared and operated the OH train and Hg SCEMs, recorded and reduced data, and assisted in sample recovery and other activities as required.
Sampling Technician	Assisted in preparation and operation of the sample trains and assisted in sample recovery and other activities as required.
Project Chemist	Performed all analytical activities at the on-site laboratory, maintained sample custody records, and shipped samples to off-site laboratory when necessary.
Sample Custodian	Maintained sample custody records, transferred samples to on-site laboratory, and assisted in sample recovery and other activities as required.
Plant Engineer	Worked with the field manager and principal investigator to facilitate data and information transfer regarding plant operations.

**Table D-10**  
**Typical Test Schedule for a 4-Week Project**

Day	Activity
1–2	Travel to site.
3–4	<p>Contact site representative, establish communications, and review unit operation; coordinate crew safety meeting; and prepare and site sampling trailers.</p> <p>Set up sample recovery and analysis area, mix fresh reagents as necessary, load sample trains for sampling, set up field blanks, and collect reagent blanks and do reagent blank analyses.</p> <p>Set up Hg SCEMs and pretreatment/conversion systems at the proper locations.</p> <p>Prepare locations for sampling (i.e., building rails) and conduct preliminary measurements.</p> <p>Leak-check sample trains.</p>
5–10	Conduct sampling activities for the first test conditions (individual responsibilities outlined in Table D-9), ensure all blanks and spiked samples meet QA/QC criteria, and ensure all Hg SCEMs are operating properly and giving good data.
11	Pack equipment, package samples for transport to the EERC, and leave site.
4–26	1 operator remains to operate Hg SCEMs for the duration of test period.
19–20	<p>Perform second round of OH analysis.</p> <p>Set up sample recovery and analysis area, mix fresh reagents as necessary, load sample trains for sampling, set up field blanks, and collect reagent blanks and do reagent blank analyses.</p> <p>Set up Hg SCEMs and pretreatment/conversion systems at the proper locations.</p> <p>Prepare locations for sampling (i.e., building rails) and conduct preliminary measurements.</p> <p>Leak-check sample trains.</p>
21–26	Conduct sampling activities for the second test conditions (individual responsibilities outlined in Table D-9), ensure all blanks and spiked samples meet QA/QC criteria, and ensure all Hg SCEMs are operating properly and giving good data.
27–28	Pack equipment, package all samples for transport to the EERC, and leave site.

Prior to sampling, 2 days were scheduled for equipment setup. Setup activities included setting up the equipment at the test locations, verifying power at the test locations, and conducting a preliminary velocity traverse (assuming the boiler is operating at or near the target test load). Final coordination with station personnel was done, and safety briefings were held.

Test team personnel arrived at the plant a minimum of 1.5 hr before the start time of the first test run on each of the days scheduled for sampling. Pretest activities included final equipment setup and leak check and verification of target unit operation and communication links between team members, team leaders, and plant personnel.

# **E**

## **SAMPLE CALCULATIONS**

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Sample calculations are included for each of the calculated parameters. Data were used from the selective catalytic reduction (SCR) unit inlet location during Day 3 (09/24/2002) from Site S6.

### **Volume of Gas Sample**

$V_m(\text{std})$  = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscf

$$V_m(\text{std}) \text{ (dscf)} = \frac{K_1 \times V_{mc} \times P_m}{T_m + 460}$$

$$V_m(\text{std}) = \frac{17.64 \times 30.485 \times 1 \times 30.02}{117.7 + 460} = 27.944 \text{ dscf}$$

Where:

$$K_1 = 17.64^\circ\text{R/in. Hg}$$

$$V_{mc} = V_m \times C_m = \text{Volume of gas sample as measured by dry gas meter corrected for meter calibration (} C_m = \text{meter calibration coefficient) (dcf)}$$

$$P_m = \text{Meter pressure (in. Hg)}$$

$$T_m = \text{Meter temperature (}^\circ\text{F)}$$

### **Volume of Water Vapor**

$V_w(\text{std})$  = Volume of water vapor in the gas sample, corrected to standard conditions, scf

$$V_w(\text{std}) \text{ (scf)} = K_2 \times \text{H}_2\text{O(g)}$$

$$V_w(\text{std}) = 0.04715 \times 58.9 = 2.777 \text{ scf}$$



Where:

$$K_2 = 0.04715 \text{ ft}^3/\text{g}$$

$$H_2O(g) = \text{Mass of liquid collected in impingers and silica gel (g)}$$

### Water Vapor in the Gas Stream

$$B_{ws} = \text{Water vapor in the gas stream, proportion by volume}$$

$$B_{ws} = \frac{V_w(\text{std})}{V_m(\text{std}) + V_w(\text{std})}$$

$$B_{ws} = \frac{2.777}{27.944 + 2.777} = 0.0904$$

### Dry Molecular Weight

$$M_d = \text{Dry molecular weight of stack gas, lb/lb-mole}$$

$$M_d (\text{lb/lb-mole}) = 0.440 \times (\%CO_2) + 0.320 \times (\%O_2) + 0.280 \times (\%N_2 + \%CO)$$

$$M_d = 0.440 \times 15.2 + 0.320 \times 4.1 + 0.280 \times 80.7 = 30.6 \text{ lb/lb-mole}$$

Where:

$$\%(CO_2, O_2, N_2, CO) = \text{Percent } (CO_2, O_2, N_2, CO) \text{ by volume, dry basis}$$

### Molecular Weight

$$M_s = \text{Molecular weight of stack gas, wet basis, lb/lb-mole}$$

$$M_s (\text{lb/lb-mole}) = M_d \times (1 - B_{ws}) + 18.0 \times B_{ws}$$

$$M_s = 30.6 \times (1 - 0.0904) + 18.0 \times 0.0904 = 29.5 \text{ lb/lb-mole}$$

### Average Stack Gas Velocity

$$V_s = \text{Average stack gas velocity, ft/sec}$$

$$V_s (\text{ft/sec}) = K_3 \times C_p \times (\Delta p)^{1/2} (\text{avg}) \times \left[ \frac{T_s + 460}{P_s \times M_s} \right]^{1/2}$$

$$V_s = 85.49 \times 0.84 \times 1.0488 \times \left[ \frac{704 + 460}{29.37 \times 29.46} \right]^{1/2} = 87.4 \text{ ft/sec}$$

Where:

$$K_3 = 85.49 \text{ ft/sec} \times \left[ \frac{\frac{\text{lb}}{\text{lb-mole}} \times \text{in.Hg}}{^\circ\text{R} \times \text{in.H}_2\text{O}} \right]^{1/2}$$

$C_p$  = Pitot tube coefficient (dimensionless)

$\Delta p$  = Velocity head of stack gas (in. Hg)

$(\Delta p)^{1/2}(\text{avg})$  = Average of the square root of  $\Delta p$  values

$T_s$  = Stack gas temperature ( $^\circ\text{F}$ )

$P_s$  = Stack pressure (in. Hg)

### Isokinetic Sampling Rate

$I$  = Percent of isokinetic sampling, %

$$I (\%) = \frac{K_4 \times (T_s + 460) \times V_m(\text{std}) \times 144}{P_s \times V_s \times A_n \times \theta \times (1 - B_{ws})}$$

$$I = \frac{0.09450 \times (704 + 460) \times 27.944 \times 144}{29.37 \times 87.4 \times 0.01986 \times 95 \times (1 - 0.0904)} = 100.5\%$$

Where:

$$K_4 = \frac{0.09450 (\text{in.Hg})(\text{min})}{^\circ\text{R} \times \text{sec}}$$

$A_n$  = Cross-sectional area of nozzle ( $\text{in.}^2$ )

$\theta$  = Total sampling time (min)

### Volume of Gas Sample Corrected to 3% O<sub>2</sub>

Vm\*(std) = Volume of gas sample measured by the dry gas meter (Vm(std)),  
\* corrected to 3% oxygen, Nm<sup>3</sup>

$$Vm^*(std) = K_5 \times Vm(std) \times \frac{21 - \%O_2}{18}$$

$$Vm^*(std) = 0.02832 \times 27.944 \times \frac{21 - 4.1}{18} = 0.743 \text{ Nm}^3$$

Where:

$$K_5 = 0.02832 \text{ m}^3/\text{ft}^3$$

### Mercury

$$Hg (\mu\text{g}/\text{Nm}^3) = \frac{\mu\text{g}}{Vm^*(std)}$$

$$Hg = \frac{2.259}{0.743} = 3.04 \mu\text{g}/\text{Nm}^3 \text{ (note: using the } Hg^0 \text{ from Day 3 SCR inlet)}$$

Particulate Hg = Sum of mercury from filter and nozzle rinse

Oxidized Hg = Sum of mercury from KCl impingers

Elemental Hg = Sum of mercury from H<sub>2</sub>O<sub>2</sub> and KMnO<sub>4</sub> impingers (note: all H<sub>2</sub>O<sub>2</sub> impinger values were nondetects). Since typically less than 5% of the elemental mercury (Hg<sup>0</sup>) is trapped in the H<sub>2</sub>O<sub>2</sub> impinger, the less-than values were not added to the total Hg<sup>0</sup>. Thus the Hg<sup>0</sup> was calculated from the values obtained from the KMnO<sub>4</sub> impingers only.

### F<sub>d</sub>

F<sub>d</sub> = Value relating gas volume to the heat content of the fuel

$$F_d (\text{dscf}/10^6 \text{ Btu}) = 10^6 \times \frac{[(K_6 \times \%H) + (K_7 \times \%C) + (K_8 \times \%S) + (K_9 \times \%N) - (K_{10} \times \%O_2)]}{HV}$$

$$F_d = 10^6 \times \frac{[(3.64 \times 5.23) + (1.53 \times 70.74) + (0.57 \times 0.86) + (0.14 \times 1.52) - (0.46 \times 9.46)]}{11,936}$$

$$= 10,357 \text{ dscf/Btu}$$

Where:

$$K_6 = 3.64 \frac{\text{dscf}}{\%H \times \text{lb}}$$

$$K_7 = 1.53 \frac{\text{dscf}}{\%C \times \text{lb}}$$

$$K_8 = 0.57 \frac{\text{dscf}}{\%S \times \text{lb}}$$

$$K_9 = 0.14 \frac{\text{dscf}}{\%N \times \text{lb}}$$

$$K_{10} = 0.46 \frac{\text{dscf}}{\%O_2 \times \text{lb}}$$

$$\text{HV} = \text{Heating value of coal (Btu/lb)}$$

$$\% (\text{H, C, S, N, O}) = \text{Percent (H, C, S, N, O) in coal (as-received from ultimate analyses)}$$